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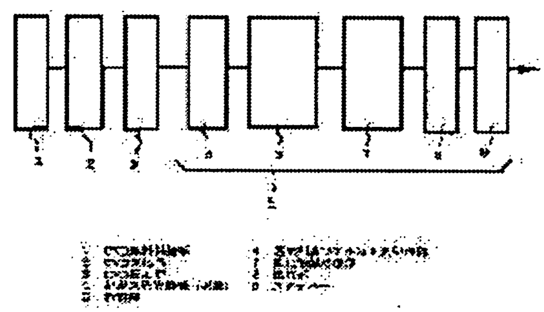
(54) WASTE GAS DETOXIFICATION APPARATUS

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a CVD waste gas detoxification apparatus for organic solution raw materials which is capable of highly efficiently detoxicating organic substances in a waste gas from CVD.
SOLUTION: A reduction and alkali treatment part 6 is installed in the CVD waste gas detoxicating apparatus 4. Especially, in the case of employing an oxidation catalyst treatment part 7 in combination with the reducing agent and the alkali agent, the detoxification effect on the waste gas is significant.



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CLAIMS

[Claim(s)]
[Claim 1] Exhaust gas damage elimination equipment constituted so that the gas which was connected to the exhaust air section of the CVD reactor using an organic compound solution raw material, and was discharged from said exhaust air section might pass the processing section by which a reducing agent and alkali chemicals have been arranged at least.
[Claim 2] Exhaust gas damage elimination equipment according to claim 1 characterized by reducing agents being at least one sort of things chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt.
[Claim 3] Exhaust gas damage elimination equipment according to claim 1 characterized by alkali chemicals being at least one sort of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide.
[Claim 4] Exhaust gas damage elimination equipment given in claim 1 characterized by being heated in the temperature requirement a reducing agent and whose alkali chemicals are 150-300 degrees C thru/or any 1 term of 3.
[Claim 5] Exhaust gas damage elimination equipment according to claim 1 characterized by having the 2nd processing section of the processing section by which a reducing agent and alkali chemicals have been arranged by which the oxidation catalyst has been arranged at least in the latter part.
[Claim 6] Exhaust gas damage elimination equipment according to claim 5 with which an oxidation catalyst is characterized by being the oxide of at least one sort of metals of Pt and the Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least.
[Claim 7] Exhaust gas damage elimination equipment according to claim 5 or 6 characterized by being heated in the temperature requirement whose oxidation catalyst is 250-450 degrees C.
[Claim 8] Exhaust gas damage elimination equipment according to claim 1 or 5 characterized by an organic compound solution raw material being the solution by which the organic compound was dissolved in the tetrahydrofuran.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] CVD (chemical vapor deposition) which this invention makes evaporate a raw material compound, and is used for membrane formation etc. -- it is related with the damage elimination equipment of the exhaust gas which occurs in connection with law. It is involved in the damage elimination equipment in the case of using the solution-like CVD raw material using an organic compound especially.
[0002]
[Description of the Prior Art] Recently, the capacitor for memory which adopted the high dielectric constant ingredient replaced with old general-purpose silicon from needs, such as improvement in the speed of devices, such as semiconductor memory, and high integration, and the strong dielectric constant ingredient is going to be developed briskly. These ingredients are multiple oxides, such as barium titanate strontium, titanic-acid lead zirconate, and tantalic acid bismuth strontium. When these oxides were formed with a CVD method, even if in many cases the present CVD raw material used as a component is a solid-state and it moreover heated it, it had the trouble of being hard to evaporate to stability. As the CVD raw material which cancels these faults, and the CVD membrane formation approach, the Japan patent No. 2799134, 2790581, etc. are confirmed, and, generally have come to be used widely [recently].
[0003] On the other hand, as exclusion equipment of the gas discharged from the above-mentioned CVD system, an example of the most general configuration is shown in drawing 4 . that drawing 4 indicated typically the flow of gassing from a CVD system to exhaust gas damage elimination equipment to be -- it is -- drawing -- setting -- 101 -- a CVD feeding system and 102 -- a CVD evaporation system and 103 -- a CVD reactor and 104 -- for the trap section and 107, as for the reaction section and 109, the adsorption section and 108 are [exhaust gas damage elimination equipment (system) and 105 / the dilution section and 106 / the combustion section and 110] scrubbers. The exhaust gas which came out from the CVD reactor 103 goes into exhaust gas damage elimination equipment 104, and is first diluted with air, nitrogen gas, etc. in the dilution section 105. Next, in the trap section 106, it is absorbed by lye etc., or it is cooled, and uptake is condensed and carried out. Subsequently, the gas constituents remaining in the adsorption section 107 are adsorbed, or decomposition clearance is carried out in the reaction section 108. With conventional common exhaust gas damage elimination equipment, the adsorption section 107 and the reaction section 108 also have united many.
[0004] Moreover, in damage elimination equipment given in JP,6-47234,A, to arrange the oxidation catalyst is considered by the adsorption section 107 at a molecular sieve and the reaction section 108. Still more generally it is melted and removed by the penetrant remover with a scrubber 110. In this case, in the case of the exhaust gas containing a lot of organic substance, the combustion section 109 is formed in the preceding paragraph of a scrubber 110, and combustion clearance may be carried out. Furthermore, as shown in JP,11-168067,A, as for a scrubber 110, either the dilution section 105 or the trap section 106 may be arranged in the preceding paragraph or the latter part, for example. Furthermore, the actual condition is devising actually attaching the filter for dust collections in many cases etc. in one part of the exhaust gas

damage elimination systems 104 variously, and used for it.
[0005]
[Problem(s) to be Solved by the Invention] However, in a CVD method, the actual condition is using the conventional general thing for semi-conductor manufacture as it is as mentioned above as the flue-gas-treatment equipment, i.e., the damage elimination equipment, at the time of making a large quantity evaporate such an organic compound comparatively, and forming membranes. In such a case, in order to process efficiently the exhaust gas containing many organic substance from a solution raw material as compared with the exhaust gas of CVD by the gas raw material currently conventionally used abundantly, it is obvious to need the energy of a large quantity considerably. moreover, in the flue-gas-treatment process in damage elimination equipment, by these organic substance's combining mutually variously, and carrying out a polymerization, the compound of the new amount of macromolecules generated and it often came out in the filter for flue gas treatment, or piping for the compound of the amount of these macromolecules to adhere so much, and to cause rapid lowering of the damage elimination engine performance. That is, the actual condition is that piping, the filter, the adsorbent, etc. started blinding and the big problem of damage elimination effectiveness and a processing life falling remarkably has arisen.
[0006] The method of contacting exhaust gas to a molecular sieve and an oxidation catalyst, and removing it as the damage elimination approach of the exhaust gas at the time of using a tetra-ethoxy silane (TEOS) etc. as a CVD raw material, is proposed so that JP,6-47234,A described above may see on the other hand. However, when such an approach was applied to the damage elimination equipment of a CVD method using the above organic compound solution raw materials, it became clear by various experiments of this invention persons that they are not necessarily effective approaches -- generation of a compound with high molecular weight is promoted on the contrary by the oxidation polymerization of the organic substance which exists so much in exhaust gas as mentioned above for the oxidation which an oxidation catalyst has, and nonconformities, such as a filter in damage elimination equipment and blinding of an adsorbent, are accelerated by it. That is, the amount of the organic substance with which it should oxidize compared with the amount of oxygen to which an oxidation catalyst exists in conditions, i.e., the inside of exhaust gas, such as temperature of exhaust gas and an ambient atmosphere, originated too in many etc., and in the original oxidative degradation operation, in order to work as an oxidation-polymerization operation nothing, the things and those [this invention] whom such nonconformity produces have guessed by accelerating macromolecule-ization by the polymerization of the organic substance.
[0007] On the other hand, when almost all gas burned conventional exhaust gas damage elimination equipment, it depended for the concentration of the injurious ingredient in gas on processing in the combustion section 109 arranged at the preceding paragraph of a scrubber 110 from the view of falling, in many cases. That is, it was processing by making exhaust gas introduce into the combustion section 109 forcibly, even if there is a problem described above. however, the maintenance of not agreeing with the image of the clean improvement in a semi-conductor from ****** which also needs combustion gas facilities (natural gas etc.), using a flame and the blinding of a burner, gas piping, etc. being serious in the combustion section, and an operating cost are expensive -- etc. -- there were also many disadvantageous points, namely, damage elimination equipment without the combustion section or the light damage elimination equipment of the burden to the combustion section was expected.
[0008] It was made in order that this invention might solve the above problems, and the polymerization of the various organic substance with which a reducing agent and alkali chemicals exist so much in exhaust gas is prevented, and this invention is proposed based on having found out that a clarification clearance operation of exhaust gas was promoted by this operation. Namely, in order to propose damage elimination equipment with the small load to the combustion section, and the damage elimination equipment which does not have the combustion section in equipment ideally, it aims at offering damage elimination equipment equipped with the processing section which has arranged a reducing agent and alkali chemicals so that exhaust gas may be contacted.

[0009]
[Means for Solving the Problem] It connects with the exhaust air section of a CVD reactor which used the organic compound solution raw material, and the exhaust gas damage elimination equipment concerning this invention is constituted so that the gas discharged from said exhaust air section may pass the processing section by which a reducing agent and alkali chemicals have been arranged at least.
[0010] In the above-mentioned exhaust gas damage elimination equipment, it specifies that reducing agents are at least one sort of things chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt.
[0011] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it specifies that alkali chemicals are at least one sort of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide.
[0012] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it is heated in the temperature requirement a reducing agent and whose alkali chemicals are 150-300 degrees C.
[0013] Furthermore, in the above-mentioned exhaust gas damage elimination equipment, it has the 2nd processing section of the processing section by which a reducing agent and alkali chemicals have been arranged by which the oxidation catalyst has been arranged at least in the latter part.
[0014] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it specifies that an oxidation catalyst is the oxide of at least one sort of metals of Pt and the Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least.
[0015] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it is heated in the temperature requirement whose oxidation catalyst is 250-450 degrees C.
[0016] In the above and exhaust gas damage elimination equipment, it specifies that the organic compound solution raw material used with the CVD reactor of the preceding paragraph is the solution by which the organic compound was dissolved in the tetrahydrofuran.
[0017]
[Embodiment of the Invention] The gestalt of 1 operation of gestalt 1. this invention of operation is explained. the invention in this application prevent the polymerization of the various organic substance with which a reducing agent and alkali chemicals exist so much in exhaust gas , arrange a reducing agent and alkali chemicals , and constitute damage elimination equipment from the exhaust air section of a CVD reactor in the exhaust gas damage elimination system which result in the blowdown section to the inside of the atmospheric air after damage elimination processing based on having find out that a clarification clearance operation of exhaust gas be promoted by this operation so that exhaust gas may be contact in one of parts .
[0018] When the oxidation catalyst is arranged rather than arrangement of a reducing agent and alkali chemicals at the downstream of emission at this time, the cleaning effect by which said polymerization inhibition operation which the former has, and the oxidation catalyst were multiplied can purify dramatically excellent dirt. That is, in the condition that macromolecule-ization by the various polymerization reactions of the organic substance does not arise under existence of a reducing agent and alkali chemicals, an oxidation catalyst demonstrates the damage elimination operation by the effective oxidative degradation to the organic substance in exhaust gas for the first time.
[0019] About a reducing agent and alkali chemicals, when heated in the 150-300-degree C temperature requirement, it turned out that it has the better damage elimination effectiveness. Although there was the damage elimination effectiveness when less than 150 degrees C, the effectiveness was not so good, and when heating temperature exceeded 300 degrees C, it checked by experiment that the pyrolysis of a reducing agent and alkali chemicals arose, and the damage elimination effectiveness might similarly decrease to a ** sake in the first [slight].
[0020] When being heated similarly about the oxidation catalyst in the 250-450-degree C temperature requirement, it checked by experiment that the better damage elimination effectiveness was demonstrated. Also in this case, in the case of the heating temperature which is less than 250 degrees C, although the damage elimination effectiveness was superior to

conventional damage elimination equipment, when that effectiveness is not necessarily remarkably good, and the crystal phase of an oxidation catalyst changed when heating temperature exceeds 450 degrees C, or a pyrolysis arose, the same experiment confirmed that the damage elimination effectiveness might similarly decrease a little.

[0021] When the reducing agents used by this invention were at least one sort of things chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt, and when alkali chemicals were similarly at least one sort of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide, the damage elimination effectiveness of better exhaust gas was demonstrated, and it became clear by experiment examination that thermal resistance is also good.

[0022] Furthermore, as an oxidation catalyst, it checked by experiment that the good exhaust gas damage elimination effectiveness was acquired by adopting the oxide of at least a kind of metal of Pt and the Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least.

[0023] According to the gestalt of this operation, the damage elimination performance test using various solution raw materials confirmed that it was applicable to the damage elimination equipment of a CVD method using various organic compound solution raw materials. Furthermore, it became clear that the especially excellent operation was demonstrated to exhaust gas in case an organic compound solution raw material is the solution by which the organic compound was dissolved in the tetrahydrofuran. That is, although the peroxide of a tetrahydrofuran in which other compounds, oxygen, and very high reactivity are shown with a CVD reaction generates, in not using this invention, it is hard to eliminate this peroxide with a well head. On the other hand, it turned out that the various organic compounds of other amounts of macromolecules which are efficient, can attain damage elimination of a peroxide if this invention is applied, therefore are produced by the reaction with a peroxide also become is also hard to be generated.

[0024] The configuration of the damage elimination equipment by the gestalt of operation of this invention is typically shown in drawing 1 . Drawing 1 shows the flow of the exhaust gas from a CVD system to the damage elimination equipment of this invention. In drawing, the supply system of the solution raw material for CVD in 1 and 2 are damage elimination equipment systems an evaporation system and 3 indicate a CVD reactor and 4 indicates examples of the configuration of this invention to be. For the dilution section and 6, as for the oxidation catalyst processing section and 8, in the system of damage elimination equipment, a reducing agent and the alkali-chemicals processing section, and 7 are [5 / the combustion section and 9] scrubbers. In this invention, the adsorption section 107 in drawing 4 which showed a reducing agent, alkali chemicals, and an oxidation catalyst in the conventional example as a configuration which applied in equipment, the reaction section 108, the combustion section 109, etc. formed a reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 instead of. Spreading and the approach of carrying out impregnation are effective in base materials, such as the honeycomb core and porosity metal which act as filters in these parts, and heat-resistant fiber. However, although these were made into what was fabricated to the pellet type, and granularity, you may install and use so that exhaust gas may pass through inside. It is ********** on a base material with an approach with the same said of alkali chemicals. It is also possible to arrange in the trap section 106 of the configuration of drawing 4 of the conventional example, or to melt into a trap solution, and to use like the means using other alkali treatment agents usually performed. Furthermore, it is possible to devise many things on an activity and to use also in this invention -- alkali chemicals can be melted in underwater [of a scrubber 110].

[0025] Drawing 2 (a) and (b) are what showed an example of the configuration of the reducing agent in the damage elimination equipment system 4 of this invention, and the alkali-chemicals processing section 6, and show the structure of a filter 17 where (a) constitutes the configuration of a reducing agent and the alkali-chemicals processing section 6, and (b) constitutes this processing section 6 among drawing among drawing. In drawing, as for the entrance line of exhaust gas, and 16, the space where the exhaust gas of reaction circles passes along 14, and 15 are the same, and outlet piping and 17 are the filters in contact with the

exhaust gas installed in the interior. The interior of a reducing agent and the alkali-chemicals processing section 6 is suitably heated by about 100-400 degrees C, exhaust gas and a filter 17 contact and decomposition of gas constituents takes place. Oxygen and air may be made to flow into this suitably, and you may use for it. The configuration of a filter 17 has become as an example as it is shown in the mimetic diagram of (b), and the porosity base material with which 18 consists of a metal porous body, heat-resistant fiber, etc., and 19 are the particles of a reducing agent and alkali chemicals. In this invention, the detailed configuration of the oxidation catalyst processing section 13 also turns into the configuration that the oxidation catalyst particle was distributed and supported by the porosity base material, in general as shown in (b) drawing.

[0026] In addition, it is not necessary to necessarily use the thing of a configuration like drawing 1 and drawing 2 , and in the damage elimination equipment of this invention, the order of arrangement of each part etc. can be changed suitably, or modification of omitting and adding can be added. Moreover, even if it has applied and arranged a reducing agent, alkali chemicals, and an oxidation catalyst to the respectively separate part and used them to it, the experiment confirmed that the damage elimination effectiveness which was excellent if only the oxidation catalyst was in the downstream of a reducing agent or alkali chemicals was acquired. Furthermore, a reducing agent and alkali chemicals checked the effective thing in the experiment which investigates the various damage elimination effectiveness, also when it used for the same part simultaneously, and also when it used for a separate part.

[0027] About the reducing agent used with the gestalt of the above-mentioned operation, alkali chemicals, and an oxidation catalyst, it is possible to form by approaches, such as vacuum evaporationo, sputtering, and ion plating, on a direct base material. Moreover, as an approach of carrying out **** (distribution, maintenance) of these matter to a filter etc., after making impregnation or its solution apply to the solution containing them, if a filter etc. is pyrolyzed at the temperature of about 200-600 degrees C, it can be easily performed in it.

[0028] Moreover, as other approaches, content distribution of a reducing agent, alkali chemicals, and the oxidation catalyst can be carried out into binding material, and the approach of applying and calcinating this and forming it on a base material, can also be used. In this case, as a binding material to be used, what is known at a heat resistant paint etc. generally [a silica sol, alumina gel, aluminum phosphate, water glass, a potassium silicate, silicone resin (organic silicon polymer), etc.] can be used.

[0029] Thus, when carrying out content distribution of a reducing agent, alkali chemicals, and the oxidation catalyst on a base material in this invention, it is not necessary to use the special coating approach, and can carry out especially by methods of applying arbitration, such as a spray method, a dip method, print processes, a spin coat method, and the roll coat method. Suitably, by desiccation at temperature and heating baking of about 100-400 degrees C, after spreading can adhere and can be formed (****).

[0030] As mentioned above, if a reducing agent and alkali chemicals prevent the polymerization of the various organic substance molecules in exhaust gas, idea ** and this invention will accomplish based on having found out that this operation also promotes a damage elimination operation of exhaust gas. Although the detailed mechanism is not clear about a polymerization inhibition operation of the organic substance, it is presumed that it originates in the following processes. That is, the oxidation polymerization of the organic substance in exhaust gas is carried out, and in the process in which the matter of the amount of macromolecules which is easy to fix that a damage is hard to be eliminated gradually is formed, the following reactions advance repeatedly, go and are presumed to be macromolecule quantification and the thing which carries out high-boiling point materialization. However, by the following formulas, in order to make it intelligible, an example is shown by using a start organic substance as a hydrocarbon. RH -> R- + H- .... (1) R- + O2 -> ROO- .... (2) ROO- + RH -> ROOH + R- ...... (3)2ROOH -> RO- + ROO + H2O .... (4) R- + R- -> R-R (polymerization) .. (5) RO- + RH -> ROH +R- ... (6) 2ROO- -> Non-radical product .... (7) [0031] However, it sets at these ceremony and is RH. For a hydrocarbon radical and H-, a hydrogen radical and ROO- are [a hydrocarbon and R-] a peroxy radical and ROOH. Hydroperoxide and RO- are [the polymer of the amount of

macromolecules and ROH of an oxy-radical and R-R] hydrides. That is, some hydrocarbons are activated by operation of heat and a reaction starts like (1) type according to it. Thereby, various matter, such as ROH, ROOH, and R-R, generates. (7) The non-radical matter generated in a formula is alcohol, an aldehyde, a ketone, etc., and these become an acid, oxy acid, an acid anhydride, ester, etc. in response to oxidation continuously, from now on, they will oxidize further and serve as the further amount matter of macromolecules. Thus, by the usual approach, it is hard to eliminate a damage, and it fixes the shape of tar, and in the shape of a particle in piping, or the generated amount matter of macromolecules serves as a ringleader which adheres to a filter etc. firmly, starts blinding, falls and checks the damage elimination engine performance. It can be guessed that the reducing agent used by this invention has accomplished the duty which controls these oxidation reaction that advances serially according to a reduction operation. It is presumed that the alkali chemicals used by this invention similarly accomplish the duty which mainly inhibits that a reaction advances [of preventing that a reaction advances more than it by neutralizing acid, such as acids (a carboxylic acid, oxy acid, etc.) generated according to progress of a reaction, and hydrolyzing the generated ester in alcohol and an acid (saponification)] more than it according to two operations. Therefore, a reducing agent or the alkali chemicals of the above-mentioned operation is [using by this invention] inadequate, and it is required to use both together.
[0032] Furthermore, if an oxidation catalyst exists when generation of the matter of the amount of macromolecules is suppressed as mentioned above, there will be no oxidation catalyst at an oxidation polymerization to the organic substance which had the polymerization controlled, it will work as an oxidative degradation operation, and it will be thought that the damage elimination effectiveness will be heightened dramatically.
[0033]
[Example] Below, a concrete example explains further at a detail.
[0034] The bipolar membrane of titanium oxide and silicon oxide was simultaneously formed on the silicon wafer using example 1. plasma-CVD equipment, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. As a raw material compound, the solution which dissolved titanium isopropoxide and a tetra-ethoxy silane in isopropyl alcohol was used. Oxygen gas was introduced by the flow rate of 200 cc in 1 minute, and membrane formation was performed for 20 minutes by setting gas pressure in a reactor to 0.5Torr(s). The dilution section 5, the combustion section 8, and a scrubber 9 were removed from the CVD damage elimination equipment configuration of this invention shown in <u>drawing 1</u> , the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 of damage elimination equipment of this invention like <u>drawing 3</u> , and the damage elimination effectiveness was examined. In drawing, in the metal porous body filter made from a nickel chrome alloy with which 17 ****(ed) a reducing agent and alkali chemicals, and 20, the entrance line to a reducing agent and the alkali-chemicals processing section and 21 ****(ed) connecting piping, 22 ****(ed) the oxidation catalyst, and the ceramic filter made from a silica alumina and 23 are outlet piping. In addition, the filter 17 applied to the metal porous body the paste which mixed the potassium silicate as the zinc powder, the ferrous sulfate (mixing ratio 1 to 1), and alkali chemicals as a reducing agent by the weight ratio of 1 to 1, and mixed the water glass (sodium silicate) as this and a binding material, and at 150 degrees C, it was calcinated for 30 minutes and it produced it. Heating retention temperature of this filter was made into 300 degrees C. In this case, the filter 22 also produced the reducing agent same instead of and the alkali chemicals as the above by the same approach, and has held and arranged them at 300 degrees C. [the oxidation catalyst]
[0035] Subsequently, for the comparison, filters 17 are the same alkali chemicals as the above, and a reducing agent, and compared the damage elimination effectiveness also about the case where produced the filter 22 as follows and an oxidation catalyst is used in order to investigate the combined effect of the oxidation catalyst in this invention. 5% of alumina was kneaded as an additive by the weight ratio to the manganese dioxide as an oxidation catalyst, and this was mixed to the methylphenyl silicone (silicone resin) as a binding material, and after adjusting

viscosity by thinner, after spreading and desiccation, at 220 degrees C, it calcinated for 40 minutes to the ceramic filter, and produced to it with the spray gun. This heating retention temperature was made into 300 degrees C. About the exhaust gas damage elimination effectiveness of the damage elimination equipment of two sorts of this inventions produced as mentioned above, a gas chromatograph, a total-organic-carbon meter, and infrared type gas-concentration-measurement equipment (all are commercial items) were used, and the concentration of the tetra-ethoxy silane in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing, total organic carbon, and a carbon monoxide was measured and evaluated, respectively. A result is shown in a table 1 with the result of the example 1 of a comparison.
[0036] Membranes were formed on the same conditions with the CVD method completely like the example of comparison 1. example 1, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where only the ceramic filter which ****(ed) the manganese-dioxide system catalyst used in the example 1 is arranged and (heating temperature of 300 degrees C) used. This result is shown in a table 1 with the result of an example 1. Two sorts of damage elimination equipments [each] of this invention had the damage elimination effectiveness better than what used only the conventional oxidation catalyst over each exhaust gas component so that clearly from a table 1. When an oxidation catalyst was especially used together in addition to the reducing agent and alkali chemicals of this invention, it became clear that the damage elimination effectiveness was extremely excellent. According to the example 1, it decreases with the processed exhaust gas, for example, a carbon monoxide, without the combustion section 8 in drawing 1 below at the threshold limit value which can be discharged. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.
[0037]
[A table 1]

表１　除害効果の比較

	ガス濃度		
	テトラエトキシシラン (ppm)	全有機体炭素 (ppm)	一酸化炭素 (ppm)
初期CVD排ガス（無処理）	300	4500	4000
実施例１の除害装置にて処理後（還元剤、アルカリ剤）	50	350	40
実施例１の除害装置にて処理後（還元剤、アルカリ剤に酸化触媒併用）	10	50	25
比較例１の除害装置にて処理後	50	400	60

[0038] The titanic-acid lead zirconate system thin film was formed on the silicon wafer using the example 2. hot wall type large-sized CVD system, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. What dissolved these in diethylether and the mixed solvent of butyl acetate by the predetermined ratio was used as a solution raw material, using lead dipivaloylmethanato, zirconium tertiary butoxide, and titanium acetylacetonate as a raw material compound. Reactant gas is oxygen and performed membrane formation for 15 minutes by setting reactor internal pressure to 8Torr(s). Like the example 1, the dilution section 5, the combustion section 8, and a scrubber 9 were removed from the CVD damage elimination equipment configuration of **** this invention to drawing 1 , it led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 of damage elimination equipment of this invention

which show the exhaust gas from a CVD reactor to drawing 3 , and the damage elimination effectiveness was examined. In addition, in this case, the filter 17 mixed the sodium hydrogensulfite as a reducing agent, and the sodium carbonate as alkali chemicals by the weight ratio of 2 to 1, and the paste mixed with a small amount of silicon dioxide and talc (both additive for adhesive improvement) was applied to the metal porous body, and it dried, and at 350 degrees C, the methylphenyl silicone as this and a binding material was calcinated for 30 minutes, and it produced it. Heating temperature of this filter was made into 250 degrees C. Heating temperature was made into 400 degrees C with the filter 22, using platinum (Pt) as an oxidation catalyst. In this case, after repeating the process which applies 10% ethanol solution of chloroplatinic acid to a ceramic filter, and is dried 3 times, at 130 degrees C, it calcinated for 20 minutes and produced. About the treatment effect of the damage elimination equipment of this invention, a total-organic-carbon meter and infrared type gas-concentration-measurement equipment were used, and the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing and a carbon monoxide was measured and evaluated, respectively. A result is shown in a table 2 with the result of the example 2 of a comparison.

[0039] Completely like the example of comparison 2. example 2, the titanic-acid lead zirconate system thin film was formed on the same conditions with the CVD method, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where have heated and arranged only the ceramic filter which ****(ed) the platinum catalyst used in the example 2 at 400 degrees C, and it is used for them. This result is shown in a table 2 with the result of an example 2. The exclusion equipment of this invention which used the oxidation catalyst together in addition to a reducing agent and alkali chemicals had the damage elimination effectiveness far better than what used only the conventional oxidation catalyst over each exhaust gas component like the example 1 also in this case so that clearly from a table 2. According to the example 2, even threshold limit value decreases with the processed exhaust gas, for example, a carbon monoxide. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.

[0040]

[A table 2]

表２　除害効果の比較

	ガス濃度	
	全有機体炭素 (ppm)	一酸化炭素 (ppm)
初期 CVD 排ガス (無処理)	5500	4500
実施例２の除害装置にて処理後	100	50
比較例２の除害装置にて処理後	600	80

[0041] The experiment which investigates what kind of thing is suitable as the reducing agent used by example 3. this invention, alkali chemicals, and an oxidation catalyst was conducted. The same experiment as examples 1 and 2 was conducted instead of the potassium silicate and sodium carbonate which were used instead of the zinc used in the examples 1 and 2, the ferrous sulfate, and the sodium hydrogensulfite in the examples 1 and 2 also as alkali chemicals as a reducing agent using various kinds of things using various kinds of things. The damage elimination trial same about things other than the manganese dioxide used in the examples 1 and 2 also about the oxidation catalyst or platinum was performed, and those effectiveness was investigated. Consequently, when the reducing agent used by this invention was a kind of thing

chosen from various kinds of metal powders, a sulfite, tin<4> salt, and the 1st iron salt at least, and when alkali chemicals were similarly a kind of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide at least, it became clear that the damage elimination effectiveness of good exhaust gas as well as examples 1 and 2 was demonstrated.

[0042] Subsequently, when a kind of thing chosen from Pd or the oxide of Fe, Mn (also manganic acid ghosts other than a manganese dioxide), nickel, Co, Cr, and Cu besides the manganese dioxide of an example 1 or Pt of an example 2 was used at least as an oxidation catalyst used by this invention, the synergistic effect with a reducing agent and alkali chemicals as well as examples 1 and 2 was acquired too, and excelling in a damage elimination operation became clear.

[0043] However, about the reducing agent, the alkali chemicals, and the oxidation catalyst which are used by this invention, if it is the matter which has not only the above-mentioned thing but the reducibility matter, the alkali (base) nature matter, and an oxidation catalyst operation, it can use. Although especially the ratio of both in the case of using a reducing agent and alkali chemicals simultaneously by this invention is not specified, the direction near 1 to 1 in general had [various experiments to both weight ratio] effectiveness more large [in addition,].

[0044] On the platinum film formed on the silicon wafer using the example 4. hot wall type CVD system, the barium titanate strontium system thin film was formed, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. The solution which dissolved these in the tetrahydrofuran by the predetermined ratio was used as a raw material, using barium dipivaloylmethanato, strontium dipivaloylmethanato, and titanium isopropoxy dipivaloylmethanato as a raw material compound. Reactant gas is oxygen and performed membrane formation for 30 minutes by setting reactor internal pressure to 10Torr(s). As damage elimination equipment of this invention, the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 in damage elimination equipment of the same this invention as drawing 3 , and the damage elimination effectiveness was examined. However, in this case, in drawing 3 , the filter 17 applied to the metal porous body the paste which mixed the graphite powder as a reducing agent, the sodium thiosulfate (mixing ratio 1 to 1), and the sodium aluminate as alkali chemicals by the weight ratio of 1 to 1, and fully mixed this, the butyl carbitol as a binding material, and isopropyl alcohol, and calcinated it for 30 minutes at 200 degrees C. Heating retention temperature of this filter was made into 200 degrees C. With the filter 22, heating maintenance was carried out at 350 degrees C using the oxidation catalyst which was produced and was supported with the following way. 5% of zeolite of total weight was kneaded as an additive to the copper oxide and chrome oxide (weight ratio 1 to 1) as an oxidation catalyst, and this was mixed to the water glass as a binding material, and after adjusting water viscosity, after spreading and desiccation, at 280 degrees C, it calcinated for 40 minutes to the ceramic filter, and produced to it with the spray gun. About the treatment effect of the damage elimination equipment of this invention, measurement assessment of the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing, a carbon monoxide, and a tetrahydrofuran peroxide was carried out using a total-organic-carbon meter, infrared type gas-concentration-measurement equipment, and an iodometric titration flow method, respectively. In addition, it titrated to the terminal point by the iodine sodium thiosulfate, and peroxide concentration was computed from the requirements. Under the present circumstances, all tetrahydrofuran peroxides were calculated by having assumed them to be tetrahydrofuran hydroperoxide ($C_4H_8O_3$, molecular weight 104). A result is shown in a table 3 with the result of the example 3 of a comparison.

[0045] Membranes were formed on the same conditions with the CVD method like the example of comparison 3. example 4, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where heating-held only the ceramic filter which ****(ed) the copper oxide-chrome oxide system catalyst used in the example 4 at 350 degrees C, have arranged it at

them, and it is used for them. This result is shown in a table 3 with the result of an example 4. As compared with the conventional thing, total organic carbon and carbon monoxide concentration are known by that a damage can be eliminated with a well head in the case of the damage elimination equipment of this invention so that clearly from a table 3. furthermore, in the damage elimination equipment of this invention, it became clear that the excellent damage elimination effectiveness that the concentration of a tetrahydrofuran peroxide with very high reactivity with other matter is markedly alike compared with conventional damage elimination equipment, and becomes low especially was acquired. According to the example 4, it decreases with the processed exhaust gas, for example, a carbon monoxide, below at threshold limit value. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.

[0046]

[A table 3]

表3　除害効果の比較

	ガス濃度		
	全有機体炭素(ppm)	一酸化炭素(ppm)	テトラヒドロフラン過酸化物(ppm)
初期CVD排ガス(無処理)	4500	4000	9500
実施例4の除害装置にて処理後	60	45	100
比較例3の除害装置にて処理後	400	50	1800

[0047] On the platinum film formed on the silicon wafer using the example 5. hot wall type CVD system, the tantalic acid strontium bismuth system thin film was formed, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. Using a pentaethoxy tantalum, strontium dipivaloylmethanato, and a triphenyl bismuth as a raw material compound, these were dissolved in the tetrahydrofuran by the predetermined ratio, and it considered as the solution raw material. Reactant gas is oxygen and performed membrane formation for 35 minutes by setting reactor internal pressure to 10Torr (s). As damage elimination equipment of this invention, the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 in damage elimination equipment of the same this invention as drawing 3 like the example 4, and the damage elimination effectiveness was examined. However, in this case, in drawing 3 , the filter 17 applied to the metal porous body the paste which mixed the silver (Ag) powder as a reducing agent, and the lithium carbonate as alkali chemicals by the weight ratio of 1 to 2, and fully mixed this and the aluminum phosphate (it dilutes with a phosphoric acid) as a binding material, and it was calcinated for 30 minutes and it produced it at 230 degrees C. Heating retention temperature of this filter was made into 220 degrees C. With the filter 22, the oxidation catalyst was created and supported with the following way, and heating maintenance was carried out at 280 degrees C. 5% of gamma alumina of total weight was kneaded as an additive to the manganese dioxide as an oxidation catalyst, and this was mixed to phosphoric-acid dilution aluminum phosphate the same as a binding material, and after adjusting viscosity with water, after spreading and desiccation, at 290 degrees C, it calcinated for 35 minutes to the ceramic filter, and produced to it by spin coating. the treatment effect of the damage elimination equipment of this invention -- the case of an example 4 -- the same -- the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing, and after processing, a carbon monoxide, and a tetrahydrofuran peroxide -- a total-organic-carbon meter, infrared type gas-concentration-measurement equipment, and an iodometric titration flow method were used and evaluated [measured and], respectively. A result is shown in a table 4 with the result of the example 4 of a comparison.

[0048] Membranes were formed on the same conditions with the CVD method completely like

the example of comparison 4. example 5, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where have heated and arranged only the ceramic reaction filter which ****(ed) the manganese-dioxide system catalyst used in the example 5 at 280 degrees C, and it is used for them. This result is shown in a table 4 with the result of an example 5. As compared with the conventional thing, total organic carbon and carbon monoxide concentration are known by that a damage can be eliminated with a well head in the case of the damage elimination equipment of this invention like the case of a table 3 so that clearly from a table 4. in addition, in the damage elimination equipment of this invention, it has checked that the same effectiveness as the case of the example 4 that especially the concentration of a tetrahydrofuran peroxide is markedly alike compared with conventional damage elimination equipment, and becomes low was acquired. According to the example 5, it decreases with the processed exhaust gas, for example, a carbon monoxide, below at threshold limit value. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.
[0049]
[A table 4]

表4　除害効果の比較

	ガス濃度		
	全有機体炭素(ppm)	一酸化炭素(ppm)	テトラヒドロフラン過酸化物(ppm)
初期CVD排ガス（無処理）	4500	4000	10500
実施例5の除害装置にて処理後	60	45	250
比較例4の除害装置にて処理後	400	50	4600

[0050] In the case of the example 6. example 4, the oxidation catalyst processing section 7 and a filter 22 changed the heating temperature of the filter 17 in the reducing agent and the alkali-chemicals processing section 6 which use the oxidation catalyst which carried out heating maintenance as it is as an example 4, and change from the same ingredient to 350 degrees C, and the damage elimination effectiveness of the same CVD exhaust gas as an example 4 was investigated. That is, the heating temperature of a filter 17 was changed from a room temperature to 350 degrees C, and the total-organic-carbon concentration in the exhaust gas in that case was measured like the example 4. A result is shown in a table 5. In addition, the total-organic-carbon concentration in the exhaust gas in not processing is the same as that of the case of a table 3. Although a table 5 was an example, when heated in the 150-300-degree C temperature requirement, about the reducing agent and alkali chemicals of this invention, it turned out that total-organic-carbon concentration has the very good damage elimination effectiveness of 100 ppm or less, so that it may understand from now on.
[0051]
[A table 5]

表5　還元剤およびアルカリ剤の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	室温	100	150	200	250	300	350
実施例6の除害装置にて処理後	390	200	90	60	50	35	150

[0052] In the case of the example 7. example 1, a reducing agent, the alkali-chemicals processing

section 6, and a filter 17 used the reducing agent and alkali chemicals which carried out heating maintenance at 300 degrees C as it was as the example 1, and the damage elimination effectiveness was further investigated in the detail about the case where the manganese dioxide as an oxidation catalyst is used together to this. That is, the heating temperature of the oxidation catalyst filter 22 which consists of the same ingredient arranged in the oxidation catalyst processing section 7 was changed, and the damage elimination effectiveness of the same CVD exhaust gas as an example 1 was investigated. In this case, the heating temperature of a filter 22 was changed from 200 degrees C to 500 degrees C, and the total-organic-carbon concentration in the exhaust gas in that case was measured like examples 1 and 6 etc. A result is shown in a table 6. In addition, the total-organic-carbon concentration in the exhaust gas in not processing is the same as that of the case of a table 1. Although a table 6 was an example, when heated in the 250-450-degree C temperature requirement, about the oxidation catalyst of this invention, it turned out that total-organic-carbon concentration has the very good damage elimination effectiveness of 100 ppm or less, so that it may understand from now on.

[0053]

[A table 6]

表6　酸化触媒の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	200	250	300	350	400	450	500
実施例7の除害装置にて処理後	380	100	50	30	25	15	280

[0054] The damage elimination equipment of this invention used in the example 8. examples 1-7 and the conventional damage elimination equipment used in each example of a comparison were disassembled after each experiment, and observation examination of the interior was conducted. In each example and it, and each corresponding example of a comparison, in spite of having performed the same time amount damage elimination processing, respectively, it was checked that neither an affix nor the blinding by the powder particle has arisen in each damage elimination equipment of this invention in the piping wall, the reducing agent, the alkali-chemicals filter, the oxidation catalyst filter, etc. On the other hand, in conventional damage elimination equipment, it turned out that the blinding by the generated dust particle has arisen in every place in the filter which adhesion of a tar-like product was all looked at by the piping wall, each part wall, etc., and supported the oxidation catalyst. Therefore, when it was used continuously as it is, with conventional damage elimination equipment, the throughput of exhaust gas declined rapidly and that a damage elimination processing life becomes short remarkably has presumed easily.

[0055]

[Effect of the Invention] As mentioned above, since it constituted so that the gas which the exhaust gas damage elimination equipment of this invention was connected to the exhaust air section of a CVD reactor which used the organic compound solution raw material, and was discharged from said exhaust air section might pass the processing section by which a reducing agent and alkali chemicals have been arranged at least Moreover, a reducing agent is made into at least one sort chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt. Since alkali chemicals were made into at least one sort chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide and these reducing agents and alkali chemicals were heated at 150-300 degrees C While the damage elimination effectiveness of exhaust gas improves, problems, such as blinding within damage elimination equipment, decrease, the throughput of damage elimination equipment is maintained, and the effectiveness that a damage elimination processing life is also extended is done so.

[0056] Furthermore, in the above-mentioned exhaust gas damage elimination equipment, had the 2nd processing section of the processing section by which a reducing agent and alkali chemicals have been arranged by which the oxidation catalyst has been arranged at least in the latter part.

Since the oxidation catalyst was made into at least one sort in Pt and Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least and was heated at 250-450 degrees C, the damage elimination effectiveness of exhaust gas improves further.
[0057] In the above and exhaust gas damage elimination equipment, when the solution by which the organic compound was dissolved in the tetrahydrofuran is used as an organic compound solution raw material used with the CVD reactor of the preceding paragraph, the damage elimination effectiveness which was excellent rather than it processed with conventional exhaust gas exclusion equipment is done so.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] CVD (chemical vapor deposition) which this invention makes evaporate a raw material compound, and is used for membrane formation etc. -- it is related with the damage elimination equipment of the exhaust gas which occurs in connection with law. It is involved in the damage elimination equipment in the case of using the solution-like CVD raw material using an organic compound especially.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Recently, the capacitor for memory which adopted the high dielectric constant ingredient replaced with old general-purpose silicon from needs, such as improvement in the speed of devices, such as semiconductor memory, and high integration, and the strong dielectric constant ingredient is going to be developed briskly. These ingredients are multiple oxides, such as barium titanate strontium, titanic-acid lead zirconate, and tantalic acid bismuth strontium. When these oxides were formed with a CVD method, even if in many cases the present CVD raw material used as a component is a solid-state and it moreover heated it, it had the trouble of being hard to evaporate to stability. As the CVD raw material which cancels these faults, and the CVD membrane formation approach, the Japan patent No. 2799134, 2790581, etc. are confirmed, and, generally have come to be used widely [recently].
[0003] On the other hand, as exclusion equipment of the gas discharged from the above-mentioned CVD system, an example of the most general configuration is shown in drawing 4 . that drawing 4 indicated typically the flow of gassing from a CVD system to exhaust gas damage elimination equipment to be -- it is -- drawing -- setting -- 101 -- a CVD feeding system and 102 -- a CVD evaporation system and 103 -- a CVD reactor and 104 -- for the trap section and 107, as for the reaction section and 109, the adsorption section and 108 are [exhaust gas damage elimination equipment (system) and 105 / the dilution section and 106 / the combustion section and 110] scrubbers. The exhaust gas which came out from the CVD reactor 103 goes into exhaust gas damage elimination equipment 104, and is first diluted with air, nitrogen gas, etc. in the dilution section 105. Next, in the trap section 106, it is absorbed by lye etc., or it is cooled, and uptake is condensed and carried out. Subsequently, the gas constituents remaining in the adsorption section 107 are adsorbed, or decomposition clearance is carried out in the reaction section 108. With conventional common exhaust gas damage elimination equipment, the adsorption section 107 and the reaction section 108 also have united many.
[0004] Moreover, in damage elimination equipment given in JP,6-47234,A, to arrange the oxidation catalyst is considered by the adsorption section 107 at a molecular sieve and the reaction section 108. Still more generally it is melted and removed by the penetrant remover with a scrubber 110. In this case, in the case of the exhaust gas containing a lot of organic substance, the combustion section 109 is formed in the preceding paragraph of a scrubber 110, and combustion clearance may be carried out. Furthermore, as shown in JP,11-168067,A, as for a scrubber 110, either the dilution section 105 or the trap section 106 may be arranged in the preceding paragraph or the latter part, for example. Furthermore, the actual condition is devising actually attaching the filter for dust collections in many cases etc. in one part of the exhaust gas damage elimination systems 104 variously, and used for it.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, the exhaust gas damage elimination equipment of this invention is since it constituted so that the gas which was connected to the exhaust air section of a CVD reactor which used the organic compound solution raw material, and was discharged from said exhaust air section might pass the processing section by which a reducing agent and alkali chemicals have been arranged at least, Moreover, a reducing agent is made into at least one sort chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt. Since alkali chemicals were made into at least one sort chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide and these reducing agents and alkali chemicals were heated at 150-300 degrees C While the damage elimination effectiveness of exhaust gas improves, problems, such as blinding within damage elimination equipment, decrease, the throughput of damage elimination equipment is maintained, and the effectiveness that a damage elimination processing life is also extended is done so.
[0056] Since the oxidation catalyst furthermore equipped with the 2nd processing section of the processing section by which a reducing agent and alkali chemicals have been arranged by which the oxidation catalyst has been arranged at least in the latter part in the above-mentioned exhaust gas damage elimination equipment was made into at least one sort in Pt and Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least and was heated at 250-450 degrees C The damage elimination effectiveness of exhaust gas improves further.
[0057] In the above and exhaust gas damage elimination equipment, when the solution by which the organic compound was dissolved in the tetrahydrofuran is used as an organic compound solution raw material used with the CVD reactor of the preceding paragraph, the damage elimination effectiveness which was excellent rather than it processed with conventional exhaust gas exclusion equipment is done so.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in a CVD method, the actual condition is using the conventional general thing for semi-conductor manufacture as it is as mentioned above as the flue-gas-treatment equipment, i.e., the damage elimination equipment, at the time of making a large quantity evaporate such an organic compound comparatively, and forming membranes. In such a case, in order to process efficiently the exhaust gas containing many organic substance from a solution raw material as compared with the exhaust gas of CVD by the gas raw material currently conventionally used abundantly, it is obvious to need the energy of a large quantity considerably. moreover, in the flue-gas-treatment process in damage elimination equipment, by these organic substance's combining mutually variously, and carrying out a polymerization, the compound of the new amount of macromolecules generated and it often came out in the filter for flue gas treatment, or piping for the compound of the amount of these macromolecules to adhere so much, and to cause rapid lowering of the damage elimination engine performance. That is, the actual condition is that piping, the filter, the adsorbent, etc. started blinding and the big problem of damage elimination effectiveness and a processing life falling remarkably has arisen.
[0006] The method of contacting exhaust gas to a molecular sieve and an oxidation catalyst, and removing it as the damage elimination approach of the exhaust gas at the time of using a tetra-ethoxy silane (TEOS) etc. as a CVD raw material, is proposed so that JP,6-47234,A described above may see on the other hand. However, when such an approach was applied to the damage elimination equipment of a CVD method using the above organic compound solution raw materials, it became clear by various experiments of this invention persons that they are not necessarily effective approaches -- generation of a compound with high molecular weight is promoted on the contrary by the oxidation polymerization of the organic substance which exists so much in exhaust gas as mentioned above for the oxidation which an oxidation catalyst has, and nonconformities, such as a filter in damage elimination equipment and blinding of an adsorbent, are accelerated by it. That is, the amount of the organic substance with which it should oxidize compared with the amount of oxygen to which an oxidation catalyst exists in conditions, i.e., the inside of exhaust gas, such as temperature of exhaust gas and an ambient atmosphere, originated too in many etc., and in the original oxidative degradation operation, in order to work as an oxidation-polymerization operation nothing, the things and those [this invention] whom such nonconformity produces have guessed by accelerating macromolecule-ization by the polymerization of the organic substance.
[0007] On the other hand, when almost all gas burned conventional exhaust gas damage elimination equipment, it depended for the concentration of the injurious ingredient in gas on processing in the combustion section 109 arranged at the preceding paragraph of a scrubber 110 from the view of falling, in many cases. That is, it was processing by making exhaust gas introduce into the combustion section 109 forcibly, even if there is a problem described above. however, the maintenance of not agreeing with the image of the clean improvement in a semi-conductor from ****** which also needs combustion gas facilities (natural gas etc.), using a flame and the blinding of a burner, gas piping, etc. being serious in the combustion section, and an operating cost are expensive -- etc. -- there were also many disadvantageous points,

namely, damage elimination equipment without the combustion section or the light damage elimination equipment of the burden to the combustion section was expected.
[0008] It was made in order that this invention might solve the above problems, and the polymerization of the various organic substance with which a reducing agent and alkali chemicals exist so much in exhaust gas is prevented, and this invention is proposed based on having found out that a clarification clearance operation of exhaust gas was promoted by this operation. Namely, in order to propose damage elimination equipment with the small load to the combustion section, and the damage elimination equipment which does not have the combustion section in equipment ideally, it aims at offering damage elimination equipment equipped with the processing section which has arranged a reducing agent and alkali chemicals so that exhaust gas may be contacted.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] It connects with the exhaust air section of a CVD reactor which used the organic compound solution raw material, and the exhaust gas damage elimination equipment concerning this invention is constituted so that the gas discharged from said exhaust air section may pass the processing section by which a reducing agent and alkali chemicals have been arranged at least.
[0010] In the above-mentioned exhaust gas damage elimination equipment, it specifies that reducing agents are at least one sort of things chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt.
[0011] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it specifies that alkali chemicals are at least one sort of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide.
[0012] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it is heated in the temperature requirement a reducing agent and whose alkali chemicals are 150-300 degrees C.
[0013] Furthermore, in the above-mentioned exhaust gas damage elimination equipment, it has the 2nd processing section of the processing section by which a reducing agent and alkali chemicals have been arranged by which the oxidation catalyst has been arranged at least in the latter part.
[0014] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it specifies that an oxidation catalyst is the oxide of at least one sort of metals of Pt and the Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least.
[0015] Moreover, in the above-mentioned exhaust gas damage elimination equipment, it is heated in the temperature requirement whose oxidation catalyst is 250-450 degrees C.
[0016] In the above and exhaust gas damage elimination equipment, it specifies that the organic compound solution raw material used with the CVD reactor of the preceding paragraph is the solution by which the organic compound was dissolved in the tetrahydrofuran.
[0017]
[Embodiment of the Invention] The gestalt of 1 operation of gestalt 1. this invention of operation is explained. the invention in this application prevent the polymerization of the various organic substance with which a reducing agent and alkali chemicals exist so much in exhaust gas , arrange a reducing agent and alkali chemicals , and constitute damage elimination equipment from the exhaust air section of a CVD reactor in the exhaust gas damage elimination system which result in the blowdown section to the inside of the atmospheric air after damage elimination processing based on having find out that a clarification clearance operation of exhaust gas be promoted by this operation so that exhaust gas may be contact in one of parts .
[0018] When the oxidation catalyst is arranged rather than arrangement of a reducing agent and alkali chemicals at the downstream of emission at this time, the cleaning effect by which said polymerization inhibition operation which the former has, and the oxidation catalyst were multiplied can purify dramatically excellent dirt. That is, in the condition that macromolecule-ization by the various polymerization reactions of the organic substance does not arise under existence of a reducing agent and alkali chemicals, an oxidation catalyst demonstrates the

damage elimination operation by the effective oxidative degradation to the organic substance in exhaust gas for the first time.
[0019] About a reducing agent and alkali chemicals, when heated in the 150-300-degree C temperature requirement, it turned out that it has the better damage elimination effectiveness. Although there was the damage elimination effectiveness when less than 150 degrees C, the effectiveness was not so good, and when heating temperature exceeded 300 degrees C, it checked by experiment that the pyrolysis of a reducing agent and alkali chemicals arose, and the damage elimination effectiveness might similarly decrease to a ** sake in the first [slight].
[0020] When being heated similarly about the oxidation catalyst in the 250-450-degree C temperature requirement, it checked by experiment that the better damage elimination effectiveness was demonstrated. Also in this case, in the case of the heating temperature which is less than 250 degrees C, although the damage elimination effectiveness was superior to conventional damage elimination equipment, when that effectiveness is not necessarily remarkably good, and the crystal phase of an oxidation catalyst changed when heating temperature exceeds 450 degrees C, or a pyrolysis arose, the same experiment confirmed that the damage elimination effectiveness might similarly decrease a little.
[0021] When the reducing agents used by this invention were at least one sort of things chosen from a metal powder, a sulfite, tin<4> salt, and the 1st iron salt, and when alkali chemicals were similarly at least one sort of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide, the damage elimination effectiveness of better exhaust gas was demonstrated, and it became clear by experiment examination that thermal resistance is also good.
[0022] Furthermore, as an oxidation catalyst, it checked by experiment that the good exhaust gas damage elimination effectiveness was acquired by adopting the oxide of at least a kind of metal of Pt and the Pd chosen from a kind, and/or Fe, Mn, nickel, Co, Cu and Cr at least.
[0023] According to the gestalt of this operation, the damage elimination performance test using various solution raw materials confirmed that it was applicable to the damage elimination equipment of a CVD method using various organic compound solution raw materials. Furthermore, it became clear that the especially excellent operation was demonstrated to exhaust gas in case an organic compound solution raw material is the solution by which the organic compound was dissolved in the tetrahydrofuran. That is, although the peroxide of a tetrahydrofuran in which other compounds, oxygen, and very high reactivity are shown with a CVD reaction generates, in not using this invention, it is hard to eliminate this peroxide with a well head. On the other hand, it turned out that the various organic compounds of other amounts of macromolecules which are efficient, can attain damage elimination of a peroxide if this invention is applied, therefore are produced by the reaction with a peroxide also become is also hard to be generated.
[0024] The configuration of the damage elimination equipment by the gestalt of operation of this invention is typically shown in drawing 1 . Drawing 1 shows the flow of the exhaust gas from a CVD system to the damage elimination equipment of this invention. In drawing, the supply system of the solution raw material for CVD in 1 and 2 are damage elimination equipment systems an evaporation system and 3 indicate a CVD reactor and 4 indicates examples of the configuration of this invention to be. For the dilution section and 6, as for the oxidation catalyst processing section and 8, in the system of damage elimination equipment, a reducing agent and the alkali-chemicals processing section, and 7 are [5 / the combustion section and 9] scrubbers. In this invention, the adsorption section 107 in drawing 4 which showed a reducing agent, alkali chemicals, and an oxidation catalyst in the conventional example as a configuration which applied in equipment, the reaction section 108, the combustion section 109, etc. formed a reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 instead of. Spreading and the approach of carrying out impregnation are effective in base materials, such as the honeycomb core and porosity metal which act as filters in these parts, and heat-resistant fiber. However, although these were made into what was fabricated to the pellet type, and granularity, you may install and use so that exhaust gas may pass through inside. It is ********** on a base material with an approach with the same said of alkali

chemicals. It is also possible to arrange in the trap section 106 of the configuration of drawing 4 of the conventional example, or to melt into a trap solution, and to use like the means using other alkali treatment agents usually performed. Furthermore, it is possible to devise many things on an activity and to use also in this invention -- alkali chemicals can be melted in underwater [of a scrubber 110].

[0025] Drawing 2 (a) and (b) are what showed an example of the configuration of the reducing agent in the damage elimination equipment system 4 of this invention, and the alkali-chemicals processing section 6, and show the structure of a filter 17 where (a) constitutes the configuration of a reducing agent and the alkali-chemicals processing section 6, and (b) constitutes this processing section 6 among drawing among drawing. In drawing, as for the entrance line of exhaust gas, and 16, the space where the exhaust gas of reaction circles passes along 14, and 15 are the same, and outlet piping and 17 are the filters in contact with the exhaust gas installed in the interior. The interior of a reducing agent and the alkali-chemicals processing section 6 is suitably heated by about 100-400 degrees C, exhaust gas and a filter 17 contact and decomposition of gas constituents takes place. Oxygen and air may be made to flow into this suitably, and you may use for it. The configuration of a filter 17 has become as an example as it is shown in the mimetic diagram of (b), and the porosity base material with which 18 consists of a metal porous body, heat-resistant fiber, etc., and 19 are the particles of a reducing agent and alkali chemicals. In this invention, the detailed configuration of the oxidation catalyst processing section 13 also turns into the configuration that the oxidation catalyst particle was distributed and supported by the porosity base material, in general as shown in (b) drawing.

[0026] In addition, it is not necessary to necessarily use the thing of a configuration like drawing 1 and drawing 2 , and in the damage elimination equipment of this invention, the order of arrangement of each part etc. can be changed suitably, or modification of omitting and adding can be added. Moreover, even if it has applied and arranged a reducing agent, alkali chemicals, and an oxidation catalyst to the respectively separate part and used them to it, the experiment confirmed that the damage elimination effectiveness which was excellent if only the oxidation catalyst was in the downstream of a reducing agent or alkali chemicals was acquired. Furthermore, a reducing agent and alkali chemicals checked the effective thing in the experiment which investigates the various damage elimination effectiveness, also when it used for the same part simultaneously, and also when it used for a separate part.

[0027] About the reducing agent used with the gestalt of the above-mentioned operation, alkali chemicals, and an oxidation catalyst, it is possible to form by approaches, such as vacuum evaporationo, sputtering, and ion plating, on a direct base material. Moreover, as an approach of carrying out **** (distribution, maintenance) of these matter to a filter etc., after making impregnation or its solution apply to the solution containing them, if a filter etc. is pyrolyzed at the temperature of about 200-600 degrees C, it can be easily performed in it.

[0028] Moreover, as other approaches, content distribution of a reducing agent, alkali chemicals, and the oxidation catalyst can be carried out into binding material, and the approach of applying and calcinating this and forming it on a base material, can also be used. In this case, as a binding material to be used, what is known at a heat resistant paint etc. generally [a silica sol, alumina gel, aluminum phosphate, water glass, a potassium silicate, silicone resin (organic silicon polymer), etc.] can be used.

[0029] Thus, when carrying out content distribution of a reducing agent, alkali chemicals, and the oxidation catalyst on a base material in this invention, it is not necessary to use the special coating approach, and can carry out especially by methods of applying arbitration, such as a spray method, a dip method, print processes, a spin coat method, and the roll coat method. Suitably, by desiccation at temperature and heating baking of about 100-400 degrees C, after spreading can adhere and can be formed (****).

[0030] As mentioned above, if a reducing agent and alkali chemicals prevent the polymerization of the various organic substance molecules in exhaust gas, idea ** and this invention will accomplish based on having found out that this operation also promotes a damage elimination operation of exhaust gas. Although the detailed mechanism is not clear about a polymerization

inhibition operation of the organic substance, it is presumed that it originates in the following processes. That is, the oxidation polymerization of the organic substance in exhaust gas is carried out, and in the process in which the matter of the amount of macromolecules which is easy to fix that a damage is hard to be eliminated gradually is formed, the following reactions advance repeatedly, go and are presumed to be macromolecule quantification and the thing which carries out high-boiling point materialization. However, by the following formulas, in order to make it intelligible, an example is shown by using a start organic substance as a hydrocarbon. RH -> R- + H- .... (1) R- + O2 -> ROO- .... (2) ROO- + RH -> ROOH + R- ...... (3)2ROOH -> RO- + ROO + H2O .... (4) R- + R- -> R-R (polymerization) .. (5) RO- + RH -> ROH +R- ... (6) 2ROO- -> Non-radical product .... (7) [0031] However, it sets at these ceremony and is RH. For a hydrocarbon radical and H-, a hydrogen radical and ROO- are [a hydrocarbon and R-] a peroxy radical and ROOH. Hydroperoxide and RO- are [the polymer of the amount of macromolecules and ROH of an oxy-radical and R-R] hydrides. That is, some hydrocarbons are activated by operation of heat and a reaction starts like (1) type according to it. Thereby, various matter, such as ROH, ROOH, and R-R, generates. (7) The non-radical matter generated in a formula is alcohol, an aldehyde, a ketone, etc., and these become an acid, oxy acid, an acid anhydride, ester, etc. in response to oxidation continuously, from now on, they will oxidize further and serve as the further amount matter of macromolecules. Thus, by the usual approach, it is hard to eliminate a damage, and it fixes the shape of tar, and in the shape of a particle in piping, or the generated amount matter of macromolecules serves as a ringleader which adheres to a filter etc. firmly, starts blinding, falls and checks the damage elimination engine performance. It can be guessed that the reducing agent used by this invention has accomplished the duty which controls these oxidation reaction that advances serially according to a reduction operation. It is presumed that the alkali chemicals used by this invention similarly accomplish the duty which mainly inhibits that a reaction advances [of preventing that a reaction advances more than it by neutralizing acid, such as acids (a carboxylic acid, oxy acid, etc.) generated according to progress of a reaction, and hydrolyzing the generated ester in alcohol and an acid (saponification)] more than it according to two operations. Therefore, a reducing agent or the alkali chemicals of the above-mentioned operation is [using by this invention] inadequate, and it is required to use both together.

[0032] Furthermore, if an oxidation catalyst exists when generation of the matter of the amount of macromolecules is suppressed as mentioned above, there will be no oxidation catalyst at an oxidation polymerization to the organic substance which had the polymerization controlled, it will work as an oxidative degradation operation, and it will be thought that the damage elimination effectiveness will be heightened dramatically.

[Translation done.]

EXAMPLE

[Example] Below, a concrete example explains further at a detail.
[0034] The bipolar membrane of titanium oxide and silicon oxide was simultaneously formed on the silicon wafer using example 1. plasma-CVD equipment, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. As a raw material compound, the solution which dissolved titanium isopropoxide and a tetra-ethoxy silane in isopropyl alcohol was used. Oxygen gas was introduced by the flow rate of 200 cc in 1 minute, and membrane formation was performed for 20 minutes by setting gas pressure in a reactor to 0.5Torr(s). The dilution section 5, the combustion section 8, and a scrubber 9 were removed from the CVD damage elimination equipment configuration of this invention shown in drawing 1 , the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 of damage elimination equipment of this invention like drawing 3 , and the damage elimination effectiveness was examined. In drawing, in the metal porous body filter made from a nickel chrome alloy with which 17 ****(ed) a reducing agent and alkali chemicals, and 20, the entrance line to a reducing agent and the alkali-chemicals processing section and 21 ****(ed) connecting piping, 22 ****(ed) the oxidation catalyst, and the ceramic filter made from a silica alumina and 23 are outlet piping. In addition, the filter 17 applied to the metal porous body the paste which mixed the potassium silicate as the zinc powder, the ferrous sulfate (mixing ratio 1 to 1), and alkali chemicals as a reducing agent by the weight ratio of 1 to 1, and mixed the water glass (sodium silicate) as this and a binding material, and at 150 degrees C, it was calcinated for 30 minutes and it produced it. Heating retention temperature of this filter was made into 300 degrees C. In this case, the filter 22 also produced the reducing agent same instead of and the alkali chemicals as the above by the same approach, and has held and arranged them at 300 degrees C. [the oxidation catalyst]
[0035] Subsequently, for the comparison, filters 17 are the same alkali chemicals as the above, and a reducing agent, and compared the damage elimination effectiveness also about the case where produced the filter 22 as follows and an oxidation catalyst is used in order to investigate the combined effect of the oxidation catalyst in this invention. 5% of alumina was kneaded as an additive by the weight ratio to the manganese dioxide as an oxidation catalyst, and this was mixed to the methylphenyl silicone (silicone resin) as a binding material, and after adjusting viscosity by thinner, after spreading and desiccation, at 220 degrees C, it calcinated for 40 minutes to the ceramic filter, and produced to it with the spray gun. This heating retention temperature was made into 300 degrees C. About the exhaust gas damage elimination effectiveness of the damage elimination equipment of two sorts of this inventions produced as mentioned above, a gas chromatograph, a total-organic-carbon meter, and infrared type gas-concentration-measurement equipment (all are commercial items) were used, and the concentration of the tetra-ethoxy silane in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing, total organic carbon, and a carbon monoxide was measured and evaluated, respectively. A result is shown in a table 1 with the result of the example 1 of a comparison.
[0036] Membranes were formed on the same conditions with the CVD method completely like

the example of comparison 1. example 1, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where only the ceramic filter which ****(ed) the manganese-dioxide system catalyst used in the example 1 is arranged and (heating temperature of 300 degrees C) used. This result is shown in a table 1 with the result of an example 1. Two sorts of damage elimination equipments [each] of this invention had the damage elimination effectiveness better than what used only the conventional oxidation catalyst over each exhaust gas component so that clearly from a table 1. When an oxidation catalyst was especially used together in addition to the reducing agent and alkali chemicals of this invention, it became clear that the damage elimination effectiveness was extremely excellent. According to the example 1, it decreases with the processed exhaust gas, for example, a carbon monoxide, without the combustion section 8 in drawing 1 below at the threshold limit value which can be discharged. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.
[0037]
[A table 1]

表1　除害効果の比較

	ガス濃度		
	テトラエトキシシラン (ppm)	全有機体炭素 (ppm)*	一酸化炭素 (ppm)
初期CVD排ガス（未処理）	300	4500	4000
実施例1の除害装置にて処理後（還元剤、アルカリ剤）	50	350	40
実施例1の除害装置にて処理後（還元剤、アルカリ剤に酸化触媒併用）	10	50	25
比較例1の除害装置にて処理後	50	400	60

[0038] The titanic-acid lead zirconate system thin film was formed on the silicon wafer using the example 2. hot wall type large-sized CVD system, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. What dissolved these in diethylether and the mixed solvent of butyl acetate by the predetermined ratio was used as a solution raw material, using lead dipivaloylmethanato, zirconium tertiary butoxide, and titanium acetylacetonate as a raw material compound. Reactant gas is oxygen and performed membrane formation for 15 minutes by setting reactor internal pressure to 8Torr(s). Like the example 1, the dilution section 5, the combustion section 8, and a scrubber 9 were removed from the CVD damage elimination equipment configuration of **** this invention to drawing 1 , it led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 of damage elimination equipment of this invention which show the exhaust gas from a CVD reactor to drawing 3 , and the damage elimination effectiveness was examined. In addition, in this case, the filter 17 mixed the sodium hydrogensulfite as a reducing agent, and the sodium carbonate as alkali chemicals by the weight ratio of 2 to 1, and the paste mixed with a small amount of silicon dioxide and talc (both additive for adhesive improvement) was applied to the metal porous body, and it dried, and at 350 degrees C, the methylphenyl silicone as this and a binding material was calcinated for 30 minutes, and it produced it. Heating temperature of this filter was made into 250 degrees C. Heating temperature was made into 400 degrees C with the filter 22, using platinum (Pt) as an oxidation catalyst. In this case, after repeating the process which applies 10% ethanol solution of chloroplatinic acid to a ceramic filter, and is dried 3 times, at 130 degrees C, it calcinated for 20 minutes and produced. About the treatment effect of the damage elimination equipment of this

invention, a total-organic-carbon meter and infrared type gas-concentration-measurement equipment were used, and the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing and a carbon monoxide was measured and evaluated, respectively. A result is shown in a table 2 with the result of the example 2 of a comparison.

[0039] Completely like the example of comparison 2. example 2, the titanic-acid lead zirconate system thin film was formed on the same conditions with the CVD method, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where have heated and arranged only the ceramic filter which ****(ed) the platinum catalyst used in the example 2 at 400 degrees C, and it is used for them. This result is shown in a table 2 with the result of an example 2. The exclusion equipment of this invention which used the oxidation catalyst together in addition to a reducing agent and alkali chemicals had the damage elimination effectiveness far better than what used only the conventional oxidation catalyst over each exhaust gas component like the example 1 also in this case so that clearly from a table 2. According to the example 2, even threshold limit value decreases with the processed exhaust gas, for example, a carbon monoxide. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.

[0040]

[A table 2]

表２　　除害効果の比較

	ガス濃度	
	全有機体炭素 (ppm)	一酸化炭素 (ppm)
初期 CVD 排ガス （無処理）	5500	4500
実施例２の除害装置にて処理後	100	50
比較例２の除害装置にて処理後	600	80

[0041] The experiment which investigates what kind of thing is suitable as the reducing agent used by example 3. this invention, alkali chemicals, and an oxidation catalyst was conducted. The same experiment as examples 1 and 2 was conducted instead of the potassium silicate and sodium carbonate which were used instead of the zinc used in the examples 1 and 2, the ferrous sulfate, and the sodium hydrogensulfite in the examples 1 and 2 also as alkali chemicals as a reducing agent using various kinds of things using various kinds of things. The damage elimination trial same about things other than the manganese dioxide used in the examples 1 and 2 also about the oxidation catalyst or platinum was performed, and those effectiveness was investigated. Consequently, when the reducing agent used by this invention was a kind of thing chosen from various kinds of metal powders, a sulfite, tin<4> salt, and the 1st iron salt at least, and when alkali chemicals were similarly a kind of things chosen from the alkali-metal silicate, the alkali-metal carbonate, the alkali-metal aluminate, and the alkali-metal oxide at least, it became clear that the damage elimination effectiveness of good exhaust gas as well as examples 1 and 2 was demonstrated.

[0042] Subsequently, when a kind of thing chosen from Pd or the oxide of Fe, Mn (also manganic acid ghosts other than a manganese dioxide), nickel, Co, Cr, and Cu besides the manganese dioxide of an example 1 or Pt of an example 2 was used at least as an oxidation catalyst used by this invention, the synergistic effect with a reducing agent and alkali chemicals as well as examples 1 and 2 was acquired too, and excelling in a damage elimination operation became clear.

[0043] However, about the reducing agent, the alkali chemicals, and the oxidation catalyst which are used by this invention, if it is the matter which has not only the above-mentioned thing but the reducibility matter, the alkali (base) nature matter, and an oxidation catalyst operation, it can use. Although especially the ratio of both in the case of using a reducing agent and alkali chemicals simultaneously by this invention is not specified, the direction near 1 to 1 in general had [various experiments to both weight ratio] effectiveness more large [in addition,].
[0044] On the platinum film formed on the silicon wafer using the example 4. hot wall type CVD system, the barium titanate strontium system thin film was formed, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. The solution which dissolved these in the tetrahydrofuran by the predetermined ratio was used as a raw material, using barium dipivaloylmethanato, strontium dipivaloylmethanato, and titanium isopropoxy dipivaloylmethanato as a raw material compound. Reactant gas is oxygen and performed membrane formation for 30 minutes by setting reactor internal pressure to 10Torr(s). As damage elimination equipment of this invention, the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 in damage elimination equipment of the same this invention as drawing 3 , and the damage elimination effectiveness was examined. However, in this case, in drawing 3 , the filter 17 applied to the metal porous body the paste which mixed the graphite powder as a reducing agent, the sodium thiosulfate (mixing ratio 1 to 1), and the sodium aluminate as alkali chemicals by the weight ratio of 1 to 1, and fully mixed this, the butyl carbitol as a binding material, and isopropyl alcohol, and calcinated it for 30 minutes at 200 degrees C. Heating retention temperature of this filter was made into 200 degrees C. With the filter 22, heating maintenance was carried out at 350 degrees C using the oxidation catalyst which was produced and was supported with the following way. 5% of zeolite of total weight was kneaded as an additive to the copper oxide and chrome oxide (weight ratio 1 to 1) as an oxidation catalyst, and this was mixed to the water glass as a binding material, and after adjusting water viscosity, after spreading and desiccation, at 280 degrees C, it calcinated for 40 minutes to the ceramic filter, and produced to it with the spray gun. About the treatment effect of the damage elimination equipment of this invention, measurement assessment of the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing and after processing, a carbon monoxide, and a tetrahydrofuran peroxide was carried out using a total-organic-carbon meter, infrared type gas-concentration-measurement equipment, and an iodometric titration flow method, respectively. In addition, it titrated to the terminal point by the iodine sodium thiosulfate, and peroxide concentration was computed from the requirements. Under the present circumstances, all tetrahydrofuran peroxides were calculated by having assumed them to be tetrahydrofuran hydroperoxide ($C_4H_8O_3$, molecular weight 104). A result is shown in a table 3 with the result of the example 3 of a comparison.
[0045] Membranes were formed on the same conditions with the CVD method like the example of comparison 3. example 4, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where heating-held only the ceramic filter which ****(ed) the copper oxide-chrome oxide system catalyst used in the example 4 at 350 degrees C, have arranged it at them, and it is used for them. This result is shown in a table 3 with the result of an example 4. As compared with the conventional thing, total organic carbon and carbon monoxide concentration are known by that a damage can be eliminated with a well head in the case of the damage elimination equipment of this invention so that clearly from a table 3. furthermore, in the damage elimination equipment of this invention, it became clear that the excellent damage elimination effectiveness that the concentration of a tetrahydrofuran peroxide with very high reactivity with other matter is markedly alike compared with conventional damage elimination equipment, and becomes low especially was acquired. According to the example 4, it decreases with the processed exhaust gas, for example, a carbon monoxide, below at threshold limit value. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of

the combustion section compared with the former, unloading of the combustion section can be planned.
[0046]
[A table 3]

表3　除害効果の比較

	ガス濃度		
	全有機体炭素 (ppm)	一酸化炭素 (ppm)	テトラヒドロフラン過酸化物(ppm)
初期CVD排ガス (無処理)	4500	4000	9500
実施例4の除害装置にて処理後	60	45	100
比較例3の除害装置にて処理後	400	50	1800

[0047] On the platinum film formed on the silicon wafer using the example 5. hot wall type CVD system, the tantalic acid strontium bismuth system thin film was formed, and the experiment which eliminates the exhaust gas in this case using the damage elimination equipment of this invention was conducted. Using a pentaethoxy tantalum, strontium dipivaloylmethanato, and a triphenyl bismuth as a raw material compound, these were dissolved in the tetrahydrofuran by the predetermined ratio, and it considered as the solution raw material. Reactant gas is oxygen and performed membrane formation for 35 minutes by setting reactor internal pressure to 10Torr (s). As damage elimination equipment of this invention, the exhaust gas from a CVD reactor was led to the reducing agent, the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 in damage elimination equipment of the same this invention as drawing 3 like the example 4, and the damage elimination effectiveness was examined. However, in this case, in drawing 3 , the filter 17 applied to the metal porous body the paste which mixed the silver (Ag) powder as a reducing agent, and the lithium carbonate as alkali chemicals by the weight ratio of 1 to 2, and fully mixed this and the aluminum phosphate (it dilutes with a phosphoric acid) as a binding material, and it was calcinated for 30 minutes and it produced it at 230 degrees C. Heating retention temperature of this filter was made into 220 degrees C. With the filter 22, the oxidation catalyst was created and supported with the following way, and heating maintenance was carried out at 280 degrees C. 5% of gamma alumina of total weight was kneaded as an additive to the manganese dioxide as an oxidation catalyst, and this was mixed to phosphoric-acid dilution aluminum phosphate the same as a binding material, and after adjusting viscosity with water, after spreading and desiccation, at 290 degrees C, it calcinated for 35 minutes to the ceramic filter, and produced to it by spin coating. the treatment effect of the damage elimination equipment of this invention -- the case of an example 4 -- the same -- the concentration of the total organic carbon in the exhaust gas in the CVD exhaust gas before damage elimination processing, and after processing, a carbon monoxide, and a tetrahydrofuran peroxide -- a total-organic-carbon meter, infrared type gas-concentration-measurement equipment, and an iodometric titration flow method were used and evaluated [measured and], respectively. A result is shown in a table 4 with the result of the example 4 of a comparison.
[0048] Membranes were formed on the same conditions with the CVD method completely like the example of comparison 4. example 5, and the damage elimination effectiveness was compared with the case of this invention instead of the reducing agent of the damage elimination equipment of drawing 3 , the alkali-chemicals processing section 6, and the oxidation catalyst processing section 7 about the case where have heated and arranged only the ceramic reaction filter which ****(ed) the manganese-dioxide system catalyst used in the example 5 at 280 degrees C, and it is used for them. This result is shown in a table 4 with the result of an example 5. As compared with the conventional thing, total organic carbon and carbon monoxide concentration are known by that a damage can be eliminated with a well head in the case of the damage elimination equipment of this invention like the case of a table 3 so that clearly from a table 4. in addition, in the damage elimination equipment of this invention, it has checked that the same effectiveness as the case of the example 4 that especially the concentration of a

tetrahydrofuran peroxide is markedly alike compared with conventional damage elimination equipment, and becomes low was acquired. According to the example 5, it decreases with the processed exhaust gas, for example, a carbon monoxide, below at threshold limit value. If the configuration of drawing 3 is applied to drawing 1 , damage elimination effectiveness will improve further. At this time, since sufficient processing is made in the preceding paragraph of the combustion section compared with the former, unloading of the combustion section can be planned.

[0049]

[A table 4]

表4　除害効果の比較

	ガス濃度		
	全有機体炭素(ppm)	一酸化炭素(ppm)	テトラヒドロフラン過酸化物(ppm)
初期CVD排ガス(無処理)	4500	4000	10500
実施例5の除害装置にて処理後	60	45	250
比較例4の除害装置にて処理後	400	50	4600

[0050] In the case of the example 6. example 4, the oxidation catalyst processing section 7 and a filter 22 changed the heating temperature of the filter 17 in the reducing agent and the alkali-chemicals processing section 6 which use the oxidation catalyst which carried out heating maintenance as it is as an example 4, and change from the same ingredient to 350 degrees C, and the damage elimination effectiveness of the same CVD exhaust gas as an example 4 was investigated. That is, the heating temperature of a filter 17 was changed from a room temperature to 350 degrees C, and the total-organic-carbon concentration in the exhaust gas in that case was measured like the example 4. A result is shown in a table 5. In addition, the total-organic-carbon concentration in the exhaust gas in not processing is the same as that of the case of a table 3. Although a table 5 was an example, when heated in the 150-300-degree C temperature requirement, about the reducing agent and alkali chemicals of this invention, it turned out that total-organic-carbon concentration has the very good damage elimination effectiveness of 100 ppm or less, so that it may understand from now on.

[0051]

[A table 5]

表5　還元剤およびアルカリ剤の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	室温	100	150	200	250	300	350
実施例6の除害装置にて処理後	390	200	90	60	50	35	150

[0052] In the case of the example 7. example 1, a reducing agent, the alkali-chemicals processing section 6, and a filter 17 used the reducing agent and alkali chemicals which carried out heating maintenance at 300 degrees C as it was as the example 1, and the damage elimination effectiveness was further investigated in the detail about the case where the manganese dioxide as an oxidation catalyst is used together to this. That is, the heating temperature of the oxidation catalyst filter 22 which consists of the same ingredient arranged in the oxidation catalyst processing section 7 was changed, and the damage elimination effectiveness of the same CVD exhaust gas as an example 1 was investigated. In this case, the heating temperature of a filter 22 was changed from 200 degrees C to 500 degrees C, and the total-organic-carbon concentration in the exhaust gas in that case was measured like examples 1 and 6 etc. A result is shown in a table 6. In addition, the total-organic-carbon concentration in the exhaust gas in not processing is the same as that of the case of a table 1. Although a table 6 was an example,

when heated in the 250-450-degree C temperature requirement, about the oxidation catalyst of this invention, it turned out that total-organic-carbon concentration has the very good damage elimination effectiveness of 100 ppm or less, so that it may understand from now on.
[0053]
[A table 6]
表6 酸化触媒の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	200	250	300	350	400	450	500
実施例7の除害装置にて処理後	380	100	50	30	25	15	280

[0054] The damage elimination equipment of this invention used in the example 8. examples 1-7 and the conventional damage elimination equipment used in each example of a comparison were disassembled after each experiment, and observation examination of the interior was conducted. In each example and it, and each corresponding example of a comparison, in spite of having performed the same time amount damage elimination processing, respectively, it was checked that neither an affix nor the blinding by the powder particle has arisen in each damage elimination equipment of this invention in the piping wall, the reducing agent, the alkali-chemicals filter, the oxidation catalyst filter, etc. On the other hand, in conventional damage elimination equipment, it turned out that the blinding by the generated dust particle has arisen in every place in the filter which adhesion of a tar-like product was all looked at by the piping wall, each part wall, etc., and supported the oxidation catalyst. Therefore, when it was used continuously as it is, with conventional damage elimination equipment, the throughput of exhaust gas declined rapidly and that a damage elimination processing life becomes short remarkably has presumed easily.
[0055]

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] That for explaining the configuration of the exhaust gas damage elimination equipment of this invention is also a mimetic diagram.
[Drawing 2] It is drawing having shown the configuration of the reducing agent in the exhaust gas damage elimination equipment of this invention, and the alkali-chemicals processing section.
[Drawing 3] It is drawing having shown the configuration of the reducing agent in the exhaust gas damage elimination equipment of this invention, the alkali-chemicals processing section, and the oxidation catalyst processing section.
[Drawing 4] It is drawing having shown the general example of a configuration of conventional exhaust gas damage elimination equipment.
[Description of Notations]
1 CVD Feeding System 2 CVD Evaporation System 3 CVD Reactor, 4 Exhaust gas damage elimination equipment (system) 5 The dilution section, a reducing agent, and the alkali-chemicals processing section 7 Oxidation catalyst processing section 8 The combustion section, 9 A scrubber, 14 Space of reaction circles, 15 The entrance line to the processing section 6, 16 Outlet piping from the processing section 6, 17 Filter installed in the interior of the processing section 6 18 Porosity base material, 19 Particle of a reducing agent and alkali chemicals 20 The entrance line to the processing section 6, 21 Connecting piping 22 The filter installed in the interior of the processing section 7, 23 Outlet piping from the processing section 7.

[Translation done.]

* NOTICES *

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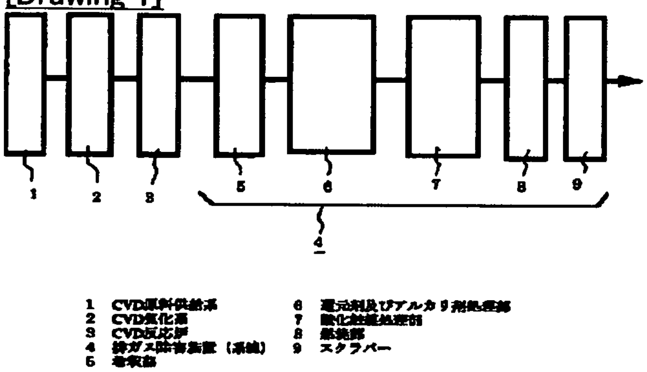
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

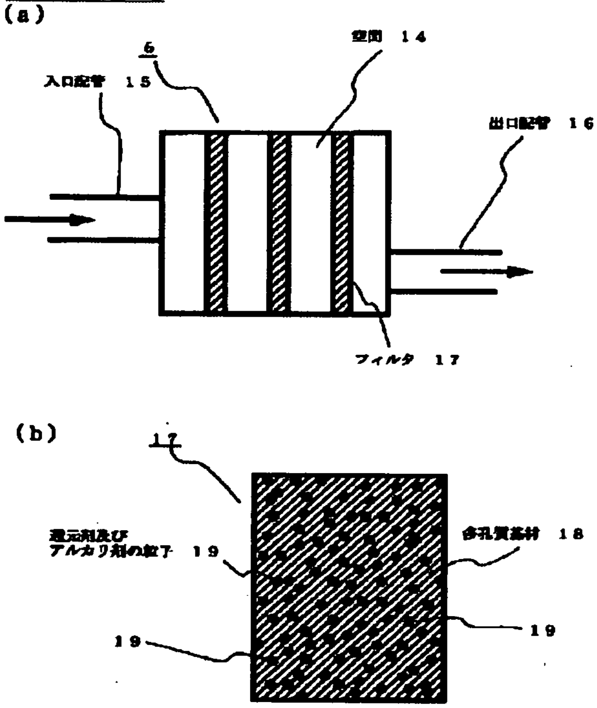
[Drawing 1]



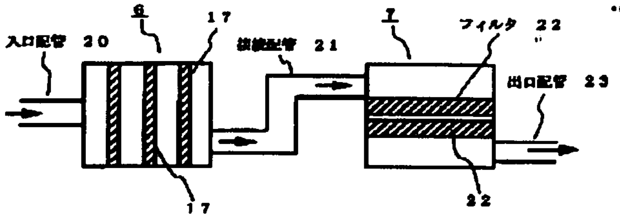
[Drawing 2]

(a)

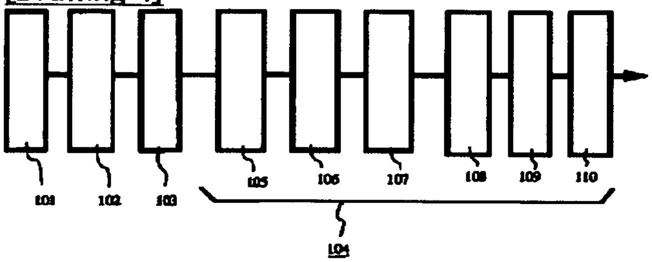
(b)



[Drawing 3]



[Drawing 4]



[Translation done.]

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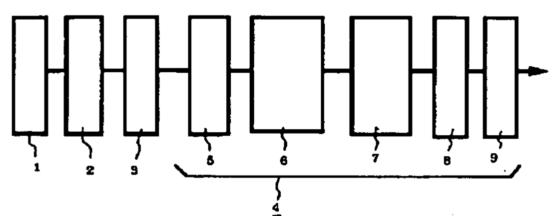
(54)【発明の名称】　排ガス除害装置

(57)【要約】
【課題】　ＣＶＤ排ガス中の有機物を高効率で除害可能な有機物溶液原料用ＣＶＤ排ガス除害装置を提供する。
【解決手段】　ＣＶＤ排ガス除害装置４において、還元剤及びアルカリ剤処理部６を配置する。特に、還元剤及びアルカリ剤に加えて酸化触媒処理部７を併用した場合において、良好な排ガスの除害効果を発揮する。



1　CVD原料供給系
2　CVD気化系
3　CVD反応炉
4　排ガス除害装置（系統）
5　希釈部
6　還元剤及びアルカリ剤処理部
7　酸化触媒処理部
8　集塵部
9　スクラバー

【特許請求の範囲】

【請求項１】 有機化合物溶液原料を用いたＣＶＤ反応炉の排気部に接続され、前記排気部から排出されたガスが少なくとも還元剤及びアルカリ剤が配置された処理部を通過するように構成された排ガス除害装置。

【請求項２】 還元剤が、金属粉、亜硫酸塩、スズ塩及び第１鉄塩の中から選ばれた少なくとも１種のものであることを特徴とする請求項１に記載の排ガス除害装置。

【請求項３】 アルカリ剤が、アルカリ金属ケイ酸塩、アルカリ金属炭酸塩、アルカリ金属アルミン酸塩及びアルカリ金属酸化物の中から選ばれた少なくとも１種のものであることを特徴とする請求項１に記載の排ガス除害装置。

【請求項４】 還元剤及びアルカリ剤が１５０～３００℃の温度範囲に加熱されることを特徴とする請求項１乃至３のいずれか１項に記載の排ガス除害装置。

【請求項５】 還元剤及びアルカリ剤の配置された処理部の少なくとも後段に酸化触媒が配置された第２の処理部を備えたことを特徴とする請求項１に記載の排ガス除害装置。

【請求項６】 酸化触媒が、Pt、Pdのうちの少なくとも一種及び／またはFe、Mn、Ni、Co、Cu及びCrから選ばれた少なくとも１種の金属の酸化物であることを特徴とする請求項５に記載の排ガス除害装置。

【請求項７】 酸化触媒が２５０～４５０℃の温度範囲に加熱されることを特徴とする請求項５または６に記載の排ガス除害装置。

【請求項８】 有機化合物溶液原料が、テトラヒドロフランに有機化合物が溶解された溶液であることを特徴とする請求項１または５に記載の排ガス除害装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、原料化合物を気化させて成膜などに用いるＣＶＤ（化学気相堆積）法に伴い発生する排ガスの除害装置に関するものである。特に、有機化合物を用いた溶液状のＣＶＤ原料を用いる場合の除害装置に係わるものである。

【０００２】

【従来の技術】最近、半導体メモリ等のデバイスの高速化や高集積化等の必要性から、これまでの汎用のシリコンに替わる高誘電率材料や強誘電率材料を採用したメモリ用のキャパシタが盛んに開発されようとしている。これらの材料は、チタン酸バリウムストロンチウム、チタン酸ジルコン酸鉛、タンタル酸ビスマスストロンチウム等のような複合酸化物である。これらの酸化物をＣＶＤ法によって成膜する場合、成分となる現行のＣＶＤ原料は多くの場合に固体であり、しかも加熱しても安定に気化しにくいという問題点があった。これらの欠点を解消するＣＶＤ原料及びＣＶＤ成膜方法として、例えば、日本国特許第２７９９１３４号ならびに同第２７９０５８１号などが有効であるとされ、最近広く一般に用いられるようになってきた。

【０００３】一方、上記ＣＶＤ装置から排出されたガスの除外装置としては、最も一般的な構成の一例を図４に示す。図４は、ＣＶＤ装置から排ガス除害装置へのガス処理の流れを模式的に示したもので、図において、１０１はＣＶＤ原料供給系、１０２はＣＶＤ気化系、１０３はＣＶＤ反応炉、１０４は排ガス除害装置（系統）、１０５は希釈部、１０６はトラップ部、１０７は吸着部、１０８は反応部、１０９は燃焼部、１１０はスクラバーである。ＣＶＤ反応炉１０３から出た排ガスは、排ガス除害装置１０４に入り、まず希釈部１０５において空気や窒素ガスなどで希釈される。次にトラップ部１０６でアルカリ液などに吸収されたり、冷却されて凝縮、捕集される。次いで吸着部１０７で残りのガス成分は吸着されたり、反応部１０８において分解除去される。従来の一般的な排ガス除害装置では、吸着部１０７と反応部１０８は一体になっているものも多い。

【０００４】また、特開平６－４７２３４号公報に記載の除害装置においては、吸着部１０７にモレキュラーシーブ及び反応部１０８に酸化触媒を配置していると考えられる。さらに一般にはスクラバー１１０で洗浄液に溶かされて除去される。この際に、多量の有機物を含む排ガスの場合にはスクラバー１１０の前段に燃焼部１０９を設けて、燃焼除去させることもある。さらに、例えば、特開平１１－１６８０６７号公報に示されるように、スクラバー１１０は、希釈部１０５またはトラップ部１０６のいずれも前段もしくは後段に配置される場合もある。さらに、排ガス除害系統１０４のいずれかの箇所に、多くの場合粉塵補集用のフィルタを取り付ける、など実際には多種多様に工夫して用いられているのが現状である。

【０００５】

【発明が解決しようとする課題】しかしＣＶＤ法において、このような有機化合物を比較的大量に気化させて成膜する際の排ガス処理装置、すなわち除害装置としては、上記のように、従来の一般の半導体製造用のものをそのまま使用しているのが現状である。このような場合、従来多用されている気体原料によるＣＶＤの排ガスと比して、溶液原料からの有機物を多く含む排ガスを効率よく処理するには、かなり大量のエネルギーを必要とすることは自明である。また、除害装置内の排ガス処理工程において、これらの有機物が多様に互いに化合したり、また重合することによって新たな高分子量の化合物が生成し、排ガス処理用のフィルタや配管内にこれら高分子量の化合物が多量に付着して除害性能の急激な低下を来すことがしばしばであった。すなわち、配管、フィルタ、吸着剤などが目詰まりを起こして除害効率や処理寿命が著しく低下するなどの大きな問題が生じているのが現状である。

【０００６】一方、上記で述べた特開平６－４７２３４号公報に見られるように、テトラエトキシシラン（TEOS）などをＣＶＤ原料として用いた場合の排ガスの除害方法として、排ガスをモレキュラーシーブ及び酸化触媒と接触させて除去する方法が提案されている。しかしこのような方法を上記のような有機化合物溶液原料を用いるＣＶＤ法の除害装置に適用すると、酸化触媒の有する酸化作用のために前記のように排ガス中に多量に存在する有機物の酸化重合によって分子量の高い化合物の生成がかえって促進され、除害装置内のフィルタや吸着剤の目詰まりなどの不具合が加速されるなど、必ずしも有効な方法ではないことが本発明者らの種々の実験により明らかになった。すなわち、酸化触媒が排ガスの温度や雰囲気等の条件によって、すなわち排ガス中に存在する酸素量に比べて酸化されるべき有機物の量が多すぎるなどに起因して、本来の酸化分解作用では無しに酸化重合作用として働くために、有機物の重合による高分子化を加速してしまうことによってこのような不具合が生じるものと本発明者らは推察している。

【０００７】一方、従来の排ガス除害装置は、殆どのガスは燃焼させればガス中の有害成分の濃度は低下するという考え方から、スクラバー１１０の前段に配置された燃焼部１０９での処理に依存することが多かった。即ち、上記で述べた問題があっても強引に燃焼部１０９に排ガスを導入させることで、処理を行っていたのである。しかし、燃焼部では火炎を使用しかつ燃焼ガス（天然ガスなど）設備も必要なたことからクリーンな半導体向上のイメージに合致しないこと、またバーナーの目詰まりやガス配管などのメンテナンスが大変なこと、運転費用が高価であるなど、不利な点も多く、即ち燃焼部を持たない除害装置あるいは燃焼部への負担の軽い除害装置が期待されていた。

【０００８】本発明は上記のような問題を解決するためになされたもので、還元剤及びアルカリ剤が排ガス中に多量に存在する種々の有機物の重合を阻止し、この作用によって排ガスの浄化除去作用が促進されることを見出したことに基づいて本発明を提案するものである。すなわち、燃焼部への負荷が小さい除害装置、理想的には装置内に燃焼部を持たない除害装置を提案するために、排気ガスと接触するように還元剤及びアルカリ剤を配置した処理部を備えた除害装置を提供することを目的とする。

【０００９】

【課題を解決するための手段】この発明に係る排ガス除害装置は、有機化合物溶液原料を用いたＣＶＤ反応炉の排気部に接続され、前記排気部から排出されたガスが少なくとも還元剤及びアルカリ剤が配置された処理部を通過するように構成されたものである。

【００１０】上記排ガス除害装置において、還元剤が、金属粉、亜硫酸塩、スズ塩及び第１鉄塩の中から選ばれた少なくとも１種のものであることを規定するものである。

【００１１】また、上記排ガス除害装置において、アルカリ剤が、アルカリ金属ケイ酸塩、アルカリ金属炭酸塩、アルカリ金属アルミン酸塩及びアルカリ金属酸化物の中から選ばれた少なくとも１種のものであることを規定するものである。

【００１２】また、上記排ガス除害装置において、還元剤及びアルカリ剤が１５０～３００℃の温度範囲に加熱されるものである。

【００１３】さらに、上記排ガス除害装置において、還元剤及びアルカリ剤の配置された処理部の少なくとも後段に酸化触媒が配置された第２の処理部を備えたものである。

【００１４】また、上記排ガス除害装置において、酸化触媒が、Pt、Pdのうちの少なくとも一種及び／またはFe、Mn、Ni、Co、Cu及びCrから選ばれた少なくとも１種の金属の酸化物であることを規定するものである。

【００１５】また、上記排ガス除害装置において、酸化触媒が２５０～４５０℃の温度範囲に加熱されるものである。

【００１６】上記、排ガス除害装置において、前段のＣＶＤ反応炉で用いられる有機化合物溶液原料が、テトラヒドロフランに有機化合物が溶解された溶液であることを規定するものである。

【００１７】

【発明の実施の形態】実施の形態１．本発明の一実施の形態について説明する。本願発明は、還元剤及びアルカリ剤が排ガス中に多量に存在する種々の有機物の重合を阻止し、この作用によって排ガスの浄化除去作用が促進されることを見出したことに基づくもので、ＣＶＤ反応炉の排気部から、除害処理後の大気中への排出部に至る排ガス除害系統において、いずれかの箇所に排気ガスと接触するように還元剤及びアルカリ剤を配置して除害装置を構成する。

【００１８】この時、還元剤及びアルカリ剤の配置よりも排ガス流の下流側に酸化触媒が配置されている場合、前者の有する前記重合阻止作用と酸化触媒の相乗された浄化作用とによって、非常に優れた汚れの浄化が行える。すなわち、還元剤及びアルカリ剤の存在下で有機物の多種多様の重合反応による高分子化が生じない状態において、酸化触媒は初めて排ガス中の有機物に対する有効な酸化分解による除害作用を発揮するのである。

【００１９】還元剤及びアルカリ剤については、１５０～３００℃の温度範囲に加熱されている場合に、より良好な除害効果を有することが分かった。１５０℃を下回る場合には、除害効果は有るものの、その効果はさほど良好ではなく、かつ加熱温度が３００℃を越える場合には還元剤及びアルカリ剤の熱分解が生じ初めるために、同じく除害効果が減少することがあることを実験により

確認した。

【００２０】酸化触媒についても、同じく２５０～４５０℃の温度範囲に加熱されている場合に、より良好な除害効果が発揮されることを実験により確認した。この場合においても、２５０℃を下回る加熱温度の場合には、従来の除害装置よりも除害効果は優れるものの、その効果は著しく良好であるというわけではなく、かつ加熱温度が４５０℃を越える場合には酸化触媒の結晶相が変化したり、または熱分解が生じることなどによって、同じく除害効果がやや減少することがあることを同様の実験により確かめた。

【００２１】本発明で用いる還元剤が、金属粉、亜硫酸塩、スズ塩及び第１鉄塩の中から選ばれた少なくとも１種のものである場合、及び同じくアルカリ剤が、アルカリ金属ケイ酸塩、アルカリ金属炭酸塩、アルカリ金属アルミン酸塩及びアルカリ金属酸化物の中から選ばれた少なくとも１種のものである場合において、より良好な排ガスの除害効果が発揮され、かつ耐熱性も良好であることが実験検討により判明した。

【００２２】さらに、酸化触媒としては、Pt、Pdのうちの少なくとも一種、及び／またはFe、Mn、Ni、Co、Cu、Crから選ばれた少なくとも一種の金属の酸化物を採用することにより、良好な排ガス除害効果が得られることを実験により確認した。

【００２３】本実施の形態によれば、種々の有機化合物溶液原料を用いたＣＶＤ法の除害装置に適用できることを各種溶液原料を用いた除害性能試験により確かめた。さらに、有機化合物溶液原料が、テトラヒドロフランに有機化合物が溶解された溶液である場合の排ガスに対して、特に優れた作用を発揮することが判明した。すなわち、ＣＶＤ反応に伴って他の化合物や酸素と非常に高い反応性を示すテトラヒドロフランの過酸化物が生成するが、本発明を用いない場合にはこの過酸化物を高効率で除害しにくい。これに対し、本発明を適用すると高効率で過酸化物の除害を達成でき、したがって過酸化物との反応によって生じる他の高分子量の種々の有機化合物も生成されにくくなることが分かった。

【００２４】本発明の実施の形態による除害装置の構成を図１中に模式的に示す。図１は、ＣＶＤ装置から本発明の除害装置への排ガスの流れを示している。図において、１はＣＶＤ用の溶液原料の供給系、２は気化系、３はＣＶＤ反応炉、４は本発明の構成の一例を示す除害装置系統である。除害装置の系統においては、５は希釈部、６は還元剤及びアルカリ剤処理部、７は酸化触媒処理部、８は燃焼部、９はスクラバーである。本発明において、還元剤、アルカリ剤、酸化触媒を装置内に適用した構成としては、従来例で示した図４における吸着部１０７、反応部１０８、燃焼部１０９などの替わりに還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７を設けた。これらの部位においてフィルタとして作用するハニカムコア、多孔質金属、耐熱繊維等の基材に塗布、含浸させる方法が有効である。ただし、これらをペレット状に成形したものや、顆粒状にしたものの中を排ガスが通過するように設置して用いても良い。アルカリ剤についても、同様の方法で基材上に担持出来る。他の通常行われているアルカリ処理剤を用いる手段と同様に、従来例の図４の構成のトラップ部１０６内に配置したり、トラップ溶液中に溶かし込んで用いることも可能である。さらには、スクラバー１１０の水中にアルカリ剤を溶かし込んでおくこともできる、など本発明においても使用上種々工夫して用いることが可能である。

【００２５】図２（ａ）、（ｂ）は本発明の除害装置系統４における還元剤及びアルカリ剤処理部６の構成の一例を示したもので、図中（ａ）は還元剤及びアルカリ剤処理部６の構成を、図中（ｂ）は該処理部６を構成するフィルタ１７の構造を示したものである。図において、１４は反応部内の排ガスが通る空間、１５は排ガスの入り口配管、１６は同じく出口配管、１７は内部に設置された排ガスと接触するフィルタである。還元剤及びアルカリ剤処理部６の内部は適宜１００～４００℃程度に加熱されており、排ガスとフィルタ１７が接触してガス成分の分解が起こるようになっている。これに適宜酸素や空気を流入させて用いても良い。フィルタ１７の構成は、一例として（ｂ）の模式図のようになっており、１８は金属多孔体や耐熱繊維等から成る多孔質基材、１９は還元剤及びアルカリ剤の粒子である。本発明では、酸化触媒処理部１３の詳細な構成も酸化触媒粒子が多孔質基材に分散、担持された概ね（ｂ）図のような構成となる。

【００２６】なお、本発明の除害装置においては、必ずしも図１及び図２のような構成のものを用いる必要はなく、適宜各部の配置順等を替えるか、省略及び追加するなどの変更を加えることが出来る。また、還元剤、アルカリ剤、酸化触媒をそれぞれ別々の部位へ適用、配置して用いても、酸化触媒が還元剤やアルカリ剤の下流側に有りさえすれば優れた除害効果が得られることを実験により確かめた。さらに還元剤とアルカリ剤は、同一部位に同時に用いた場合にも、また別々の部位に用いた場合にも有効であることを種々の除害効果を調べる実験で確認した。

【００２７】上記の実施の形態で用いる還元剤、アルカリ剤、酸化触媒については、直接基材上に蒸着、スパッタリング、イオンプレーティングなどの方法で形成することが可能である。また、これらの物質をフィルタなどに担持（分散、保持）させる方法としては、それらを含有する溶液にフィルタなどを含浸、またはその溶液を塗布させた後に、２００～６００℃程度の温度で熱分解すると簡単に行える。

【００２８】また、他の方法として、結合材中に還元剤、アルカリ剤、酸化触媒を含有分散させ、これを基材

上に塗布、焼成して形成する方法も用いることが出来る。この際に用いる結合材としては、シリカゾル、アルミナゲル、アルミニウムホスフェート、水ガラス、ケイ酸カリウム、シリコーン樹脂（有機ケイ素ポリマー）など、耐熱塗料などで一般に知られているものを用いることができる。

【００２９】このように、本発明において還元剤、アルカリ剤、酸化触媒を基材上に含有分散させる場合には、特に特殊なコーティング方法を用いる必要はなく、スプレー法、ディップ法、印刷法、スピンコート法、ロールコート法など任意の塗布法によって実施可能である。塗布後は、適宜１００～４００℃程度の温度での乾燥及び加熱焼成によって付着、形成（坦持）することができる。

【００３０】前記のように、還元剤及びアルカリ剤が排ガス中の各種有機物分子の重合を阻止すると考えらえ、本発明はこの作用が排ガスの除害作用をも促進することを見出したことに基づいて成されたものである。有機物の重合阻止作用については、その詳細なメカニズムは明らかではないが、次のようなプロセスに起因すると推定している。すなわち、排ガス中の有機物が酸化重合されて徐々に除害されにくく固着しやすい高分子量の物質が形成されていく過程においては、次のような反応が繰り返し進行して行き、高分子量化、高沸点物質化するものと推定される。ただし、以下の式では分かり易くするため、出発有機物質を炭化水素として一例を示している。

RH → R・ ＋ H・ …………(1)

R・ ＋ O_2 → ROO・ …………(2)

ROO・ ＋ RH → ROOH ＋ R・ ………(3)

2ROOH → RO・ ＋ ROO ＋ H_2O ……(4)

R・ ＋ R・ → R−R （重合） ……(5)

RO・ ＋ RH → ROH ＋R・ ………(6)

2ROO・ → 非ラジカル生成物 …………(7)

【００３１】ただし、これらの式において、RH は炭化水素、R・は炭化水素ラジカル、H・は水素ラジカル、ROO・はパーオキシラジカル、ROOH はハイドロパーオキサイド、RO・はオキシラジカル、R−Rは高分子量の重合体、ROHはハイドライドである。すなわち、熱の作用によって一部の炭化水素は活性化されて(1)式のように反応が始まる。これにより、ROH、ROOH、R−Rなどの種々の物質が生成する。(7)式において生成する非ラジカル物質はアルコール、アルデヒド、ケトンなどであり、これらは続けて酸化を受けて酸、オキシ酸、酸無水物、エステル等になり、これからさらに酸化されてさらなる高分子量物質となっていく。このようにして生成した高分子量物質が、通常の方法では除害しにくく、配管内にタール状や粒子状に固着したり、フィルタ等に強固に付着して目詰まりを起こして除害性能を低下、阻害する元凶となるものである。本発明で用いる還元剤は、還元作用によりこれらの逐次進行する酸化反応を抑制する役目を成していると推察できる。同じく、本発明で用いるアルカリ剤は、反応の進行によって生成した酸（カルボン酸、オキシ酸など）等の酸性物質を中和することによって、反応がそれ以上進行するのを阻止すること、ならびに生成したエステル類をアルコールと酸に加水分解（ケン化）することの主に二つの作用により、反応がそれ以上進行するのを抑止する役目を成すと推定している。したがって、本発明で用いるのは還元剤、アルカリ剤のいずれか一方では上記の作用が不十分であり、両者を併用することが必要である。

【００３２】さらには、上記のように高分子量の物質の生成が抑えられた場合に酸化触媒が存在すると、重合を抑制された有機物に対して酸化触媒が酸化重合では無く酸化分解作用として働き、大いに除害効果を高めることになると考えられる。

【００３３】

【実施例】以下に、具体的な実施例により、更に詳細に説明する。

【００３４】実施例１．プラズマＣＶＤ装置を使用してシリコンウエハ上に酸化チタンと酸化ケイ素の複合膜を同時に形成し、この際の排ガスを本発明の除害装置を用いて除害する実験を行った。原料化合物として、チタンイソプロポキシドとテトラエトキシシランをイソプロピルアルコールに溶解した溶液を用いた。酸素ガスを１分間に２００ｃｃの流量で導入し、反応炉内ガス圧を０．５Ｔｏｒｒとして２０分間成膜を行った。図１に示した本発明のＣＶＤ除害装置構成から希釈部５、燃焼部８及びスクラバー９を取り外し、ＣＶＤ反応炉からの排ガスを図３のような本発明の除害装置の還元剤及びアルカリ剤処理部６、及び酸化触媒処理部７に導いてその除害効果を試験した。図において、１７は還元剤及びアルカリ剤を坦持したニッケルクロム合金製金属多孔体フィルタ、２０は還元剤及びアルカリ剤処理部への入り口配管、２１は接続配管、２２は酸化触媒を坦持したしシリカアルミナ製セラミックフィルタ及び２３は出口配管である。なお、フィルタ１７は、還元剤としての亜鉛粉末と硫酸第一鉄（混合比１対１）及びアルカリ剤としてのケイ酸カリウムを１対１の重量比で混合し、これと結合材としての水ガラス（ケイ酸ナトリウム）を混合したペーストを金属多孔体に塗布し、１５０℃で３０分間焼成して作製した。このフィルタの加熱保持温度を３００℃とした。この場合においては、フィルタ２２も酸化触媒の替わりに上記と同一の還元剤及びアルカリ剤を同一の方法で作製し、３００℃に保持、配置した。

【００３５】次いで、比較のため、本発明における酸化触媒の併用効果を調べる目的で、フィルタ１７は上記と同一のアルカリ剤及び還元剤で、かつフィルタ２２を下記のように作製して酸化触媒を用いた場合についても除害効果を比べた。酸化触媒としての二酸化マンガンに重量比で５％のアルミナを添加剤として混練し、これを結

合材としてのメチルフェニルシリコーン（ケイ素樹脂）に混合し、シンナーで粘度を調節してからスプレーガンでセラミックフィルタへ塗布、乾燥後、２２０℃で４０分間焼成して作製した。この加熱保持温度は３００℃とした。以上のようにして作製した２種の本発明の除害装置の排ガス除害効果については、除害処理前のＣＶＤ排ガス中及び処理後の排ガス中におけるテトラエトキシシラン、全有機体炭素ならびに一酸化炭素の濃度を、それぞれガスクロマトグラフ、全有機体炭素計、赤外式ガス濃度測定装置（いずれも市販品）を用いて測定、評価した。結果を比較例１の結果とともに表１に示す。

【００３６】比較例１．実施例１と全く同様にしてＣＶＤ法により同一条件で成膜を行い、図３の除害装置の還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７の替わりに、実施例１で用いた二酸化マンガン系触媒を坦持したセラミックフィルタのみを配置（加熱温度３０＊＊０℃）して用いた場合について、その除害効果を本発明の場合と比較した。この結果を実施例１の結果とともに表１に示す。表１から明らかなように、本発明の２種の除害装置は、いずれも従来の酸化触媒のみを用いたものよりも各排ガス成分に対する除害効果が良好であった。特に、本発明の還元剤とアルカリ剤に加えて酸化触媒を併用した場合において、その除害効果が極めて優れることが判明した。実施例１によれば、処理された排ガス、例えば一酸化炭素では、図１中の燃焼部８を介さず排出可能な、許容濃度以下にまでに、低減されている。図３の構成を図１に適用すれば、さらに除害効率が向上する。このとき、従来と比べて燃焼部の前段で十分な処理がなされているため燃焼部の負荷軽減が図れる。

【００３７】

【表１】

表１　除害効果の比較

	ガス濃度		
	テトラエトキシシラン　(ppm)	全有機体炭素 (ppm)	一酸化炭素 (ppm)
初期 CVD 排ガス（無処理）	300	4500	4000
実施例１の除害装置にて処理後（還元剤、アルカリ剤）	60	350	40
実施例１の除害装置にて処理後（還元剤、アルカリ剤に酸化触媒併用）	10	50	25
比較例１の除害装置にて処理後	50	400	60

【００３８】実施例２．ホットウオールタイプの大型ＣＶＤ装置を使用してシリコンウエハ上にチタン酸ジルコン酸鉛系薄膜を形成し、この際の排ガスを本発明の除害装置を用いて除害する実験を行った。原料化合物として、鉛ジピバロイルメタナト、ジルコニウムターシャリーブトキシド及びチタンアセチルアセトナトを用い、これらを所定の比率でジエチルエーテルと酢酸ブチルの混合溶媒に溶解したものを溶液原料として用いた。反応ガスは酸素で、反応炉内圧力を８Ｔｏｒｒとして１５分間成膜を行った。実施例１と同様に、図１に示した本発明のＣＶＤ除害装置構成から希釈部５、燃焼部８及びスクラバー９を取り外し、ＣＶＤ反応炉からの排ガスを図３に示す本発明の除害装置の還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７に導いてその除害効果を試験した。なおこの場合、フィルタ１７は、還元剤としての亜硫酸水素ナトリウム及びアルカリ剤としての炭酸ナトリウムを２対１の重量比で混合し、これと結合材としてのメチルフェニルシリコーンを少量の二酸化珪素及びタルク（ともに付着性向上のための添加剤）とともに混合したペーストを金属多孔体に塗布、乾燥し、３５０℃で３０分間焼成して作製した。このフィルタの加熱温度は２５０℃とした。フィルタ２２では、酸化触媒として白金（Ｐｔ）を用い、加熱温度を４００℃とした。この場合、塩化白金酸の１０％エタノール溶液をセラミックフィルタに塗布して乾燥する工程を３回繰り返した後、１３０℃で２０分間焼成して作製した。本発明の除害装置の処理効果については、除害処理前のＣＶＤ排ガス中及び処理後の排ガス中の全有機体炭素ならびに一酸化炭素の濃度を、それぞれ全有機体炭素計、赤外式ガス濃度測定装置を用いて測定、評価した。結果を比較例２の結果とともに表２に示す。

【００３９】比較例２．実施例２と全く同様にして、チタン酸ジルコン酸鉛系薄膜をＣＶＤ法により同一条件で成膜し、図３の除害装置の還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７の替わりに、実施例２で用いた白金触媒を坦持したセラミックフィルタのみを４００℃に加熱、配置して用いた場合について、その除害効果を本発明の場合と比較した。この結果を実施例２の結果とともに表２に示す。表２から明らかなように、この場合も実施例１と同様に、還元剤とアルカリ剤に加えて酸化触媒を併用した本発明の除外装置は、従来の酸化触媒のみを用いたものよりも各排ガス成分に対する除害効果がはるかに良好であった。実施例２によれば、処理された排ガス、例えば一酸化炭素では、許容濃度にまでに、低減されている。図３の構成を図１に適用すれば、さらに除害効率が向上する。このとき、従来と比べて燃

焼部の前段で十分な処理がなされているため燃焼部の負荷軽減が図れる。

＊【００４０】

【表２】

表２　除害効果の比較

	ガス濃度	
	全有機体炭素 (ppm)	一酸化炭素 (ppm)
初期 CVD 排ガス（無処理）	5500	4500
実施例２の除害装置にて処理後	100	50
比較例２の除害装置にて処理後	600	80

【００４１】実施例３．本発明で用いる還元剤及びアルカリ剤ならびに酸化触媒として、どのようなものが適しているかを調べる実験を行った。還元剤として、実施例１及び２で用いた亜鉛、硫酸第１鉄、亜硫酸水素ナトリウムの代わりに各種のものを用い、アルカリ剤としても実施例１及び２で用いたケイ酸カリウム、炭酸ナトリウムの代わりに各種のものを用いて実施例１及び２と同様の実験を行った。酸化触媒についても、実施例１及び２で使用した二酸化マンガンや白金以外のものについて同様の除害試験を行って、それらの効果を調査した。その結果、本発明で用いる還元剤が、各種の金属粉、亜硫酸塩、スズ塩及び第１鉄塩の中から選ばれた少なくとも一種のものである場合、及び同じくアルカリ剤が、アルカリ金属ケイ酸塩、アルカリ金属炭酸塩、アルカリ金属アルミン酸塩及びアルカリ金属酸化物の中から選ばれた少なくとも一種のものである場合において、実施例１及び２と同様に良好な排ガスの除害効果が発揮されることが判明した。

【００４２】ついで、本発明で用いる酸化触媒として実施例１の二酸化マンガンや実施例２のPtの他に、PdまたはFe、Mn（二酸化マンガン以外のマンガン酸化物も）、Ni、Co、Cr、Cuの酸化物から選ばれた少なくとも一種のものを用いた場合に、やはり実施例１及び２と同様に還元剤及びアルカリ剤との相乗効果が得られ、除害作用に優れることが明らかとなった。

【００４３】ただし、本発明で使用する還元剤及びアルカリ剤ならびに酸化触媒については、上記のものに限らず、還元性物質、アルカリ（塩基）性物質及び酸化触媒作用を有する物質であれば用いることが出来る。なお、本発明で還元剤とアルカリ剤とを同時に用いる場合における両者の比率については特に規定するものではないが、種々の実験から両者の重量比が概ね１対１に近い方がより効果が大きかった。

【００４４】実施例４．ホットウオールタイプのＣＶＤ装置を使用してシリコンウエハ上に形成した白金膜上に、チタン酸バリウムストロンチウム系薄膜を形成し、この際の排ガスを本発明の除害装置を用いて除害する実験を行った。原料化合物として、バリウムジピバロイルメタナト、ストロンチウムジピバロイルメタナト、チタンイソプロポキシジピバロイルメタナトを用い、これらを所定比率でテトラヒドロフランに溶解した溶液を原料として用いた。反応ガスは酸素で、反応炉内圧力を１０Ｔｏｒｒとして３０分間成膜を行った。本発明の除害装置としては、ＣＶＤ反応炉からの排ガスを図３と同様の本発明の除害装置における還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７に導いてその除害効果を試験した。ただしこの場合、図３において、フィルタ１７は、還元剤としてのグラファイト粉末とチオ硫酸ナトリウム（混合比１対１）、及びアルカリ剤としてのアルミン酸ナトリウムを１対１の重量比で混合し、これと結合材としてのブチルカルビトールとイソプロピルアルコールとを十分に混合したペーストを金属多孔体に塗布し、２００℃で３０分間焼成した。このフィルタの加熱保持温度は２００℃とした。フィルタ２２では、下記の要領で作製、担持した酸化触媒を用い、３５０℃に加熱保持した。酸化触媒としての酸化銅及び酸化クロム（重量比１対１）に全重量の５％のゼオライトを添加剤として混練し、これを結合材としての水ガラスに混合し、水粘度を調節してからスプレーガンでセラミックフィルタへ塗布、乾燥後、２８０℃で４０分間焼成して作製した。本発明の除害装置の処理効果については、除害処理前のＣＶＤ排ガス中及び処理後の排ガス中の全有機体炭素、一酸化炭素ならびにテトラヒドロフラン過酸化物の濃度を、それぞれ全有機体炭素計、赤外式ガス濃度測定装置、ヨウ素滴定法を用いて測定評価した。なお、ヨウ素チオ硫酸ナトリウムで終点まで滴定してその所要量から過酸化物濃度を算出した。この際、テトラヒドロフラン過酸化物をすべてテトラヒドロフランハイドロパーオキサイド（$C_4H_8O_3$、分子量１０４）と想定して計算した。結果を比較例３の結果とともに表３に示す。

【００４５】比較例３．実施例４と同様にしてＣＶＤ法により同一条件で成膜を行い、第３図の除害装置の還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７の替わりに、実施例４で用いた酸化銅一酸化クロム系触媒を担持したセラミックフィルタのみを３５０℃に加熱保持、配置して用いた場合について、その除害効果を本発

明の場合と比較した。この結果を実施例４の結果とともに表３に示す。表３から明らかなように、本発明の除害装置の場合には、従来のものと比較すると全有機体炭素及び一酸化炭素濃度とも高効率で除害が可能であることが分かる。さらに、本発明の除害装置においては、とくに他の物質との反応性が極めて高いテトラヒドロフラン過酸化物の濃度が従来の除害装置と比べて格段に低くなるという優秀な除害効果が得られることが判明した。実施例４によれば、処理された排ガス、例えば一酸化炭素では、許容濃度以下にまでに、低減されている。図３の構成を図１に適用すれば、さらに除害効率が向上する。このとき、従来と比べて燃焼部の前段で十分な処理がなされているため燃焼部の負荷軽減が図れる。

【００４６】

【表３】

表３　除害効果の比較

	ガス濃度		
	全有機体炭素(ppm)	一酸化炭素(ppm)	テトラヒドロフラン過酸化物(ppm)
初期 CVD 排ガス（無処理）	4500	4000	9500
実施例４の除害装置にて処理後	60	45	100
比較例３の除害装置にて処理後	400	50	1800

【００４７】実施例５．ホットウオールタイプのＣＶＤ装置を使用してシリコンウエハ上に形成した白金膜上に、タンタル酸ストロンチウムビスマス系薄膜を形成し、この際の排ガスを本発明の除害装置を用いて除害する実験を行った。原料化合物として、ペンタエトキシタンタル、ストロンチウムジピバロイルメタナト、トリフェニルビスマスを用い、これらを所定比率でテトラヒドロフランに溶解して溶液原料とした。反応ガスは酸素で、反応炉内圧力を１０Ｔｏｒｒとして３５分間成膜を行った。本発明の除害装置としては、実施例４と同様にＣＶＤ反応炉からの排ガスを図３と同様の本発明の除害装置における還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７に導いてその除害効果を試験した。ただしこの場合、図３において、フィルタ１７は、還元剤としての銀（Ag）粉末及びアルカリ剤としての炭酸リチウムを１対２の重量比で混合し、これと結合材としてのアルミニウムホスフェート（リン酸で希釈）とを十分に混合したペーストを金属多孔体に塗布し、２３０℃で３０分間焼成して作製した。このフィルタの加熱保持温度は２２０℃とした。フィルタ２２では、酸化触媒を下記の要領で作成、担持し、２８０℃に加熱保持した。酸化触媒としての二酸化マンガンに全重量の５％のガンマアルミナを添加剤として混練し、これを結合材としての同じくリン酸希釈アルミニウムホスフェートに混合し、水で粘度を調節してからスピンコーティングでセラミックフィルタへ塗布、乾燥後、２９０℃で３５分間焼成して作製した。本発明の除害装置の処理効果については、実施例４の場合と同様に、除害処理前のＣＶＤ排ガス中及び処理後の排ガス中の全有機体炭素、一酸化炭素ならびにテトラヒドロフラン過酸化物の濃度、それぞれ全有機体炭素計、赤外式ガス濃度測定装置、ヨウ素滴定法を用いて測定、評価した。結果を比較例４の結果とともに表４に示す。

【００４８】比較例４．実施例５と全く同様にしてＣＶＤ法により同一条件で成膜を行い、図３の除害装置の還元剤及びアルカリ剤処理部６ならびに酸化触媒処理部７の替わりに、実施例５で用いた二酸化マンガン系触媒を坦持したセラミック反応フィルタのみを２８０℃に加熱、配置して用いた場合について、その除害効果を本発明の場合と比較した。この結果を実施例５の結果とともに表４に示す。表４から明らかなように、表３の場合と同様に本発明の除害装置の場合には、従来のものと比較すると全有機体炭素及び一酸化炭素濃度とも高効率で除害が可能であることが分かる。加えて、本発明の除害装置においては、とくにテトラヒドロフラン過酸化物の濃度が従来の除害装置と比べて格段に低くなるという実施例４の場合と同じ効果が得られることが確認できた。実施例５によれば、処理された排ガス、例えば一酸化炭素では、許容濃度以下にまでに、低減されている。図３の構成を図１に適用すれば、さらに除害効率が向上する。このとき、従来と比べて燃焼部の前段で十分な処理がなされているため燃焼部の負荷軽減が図れる。

【００４９】

【表４】

表４　除害効果の比較

	ガス濃度		
	全有機体炭素 (ppm)	一酸化炭素 (ppm)	テトラヒドロフラン過酸化物(ppm)
初期 CVD 排ガス (無処理)	4500	4000	10500
実施例５の除害装置にて処理後	60	45	250
比較例４の除害装置にて処理後	400	50	4600

【００５０】実施例６．実施例４の場合において、酸化触媒処理部７及びフィルタ２２は３５０℃に加熱保持した酸化触媒を実施例４の通りにそのまま用い、同一材料から成る還元剤及びアルカリ剤処理部６におけるフィルタ１７の加熱温度を変化させ、実施例４と同一のＣＶＤ排ガスの除害効果を調査した。すなわち、フィルタ１７の加熱温度を室温から３５０℃まで変化させ、その際の排ガス中における全有機体炭素濃度を実施例４と同様に測定した。結果を表５に示す。なお、無処理の場合の排＊ガス中の全有機体炭素濃度は、表３の場合と同一である。表５は一例であるが、これから分かるように、本発明の還元剤及びアルカリ剤については、１５０～３００℃の温度範囲に加熱されている場合に、全有機体炭素濃度が１００ppm以下という極めて良好な除害効果を有することが分かった。

【００５１】

【表５】

表５　還元剤およびアルカリ剤の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	室温	100	150	200	250	300	350
実施例６の除害装置にて処理後	390	200	90	60	50	35	150

【００５２】実施例７．実施例１の場合において、還元剤及びアルカリ剤処理部６ならびにフィルタ１７は３００℃に加熱保持した還元剤及びアルカリ剤を実施例１の通りにそのまま用い、酸化触媒としての二酸化マンガンをこれに併用した場合について、さらに詳細に除害効果を調査した。すなわち、酸化触媒処理部７内に配置した同一材料から成る酸化触媒フィルタ２２の加熱温度を変化させ、実施例１と同一のＣＶＤ排ガスの除害効果を調査した。この場合、フィルタ２２の加熱温度を２００℃から５００℃まで変化させ、その際の排ガス中の全有機※体炭素濃度を実施例１及び６などと同様に測定した。結果を表６に示す。なお、無処理の場合の排ガス中の全有機体炭素濃度は、表１の場合と同一である。表６は一例であるが、これから分かるように、本発明の酸化触媒については、２５０～４５０℃の温度範囲に加熱されている場合に、全有機体炭素濃度が１００ｐｐｍ以下という極めて良好な除害効果を有することが分かった。

【００５３】

【表６】

表６　酸化触媒の加熱温度による全有機体炭素濃度(ppm)

加熱温度(℃)	200	250	300	350	400	450	500
実施例７の除害装置にて処理後	380	100	50	30	25	15	280

【００５４】実施例８．実施例１から７で用いた本発明の除害装置、及び各比較例で用いた従来の除害装置をそれぞれの実験後に解体し、内部を観察調査した。各実施例及びそれと対応する各比較例では、それぞれ同一時間除害処理を行ったにも係わらず、本発明の各除害装置においては配管内壁や還元剤及びアルカリ剤フィルタ、ならびに酸化触媒フィルタ等に付着物や粉末粒子による目詰まりなどが生じていないことが確認された。これに対して従来の除害装置においては、いずれも配管内壁や各部内壁などにタール状生成物の付着が見られ、かつ酸化触媒を担持したフィルタなどには生成した粉塵粒子による目詰まりが各所で生じていることが分かった。したがって、このまま連続して使用すると、従来の除害装置では排ガスの処理能力が急激に低下し、著しく除害処理寿命が短くなることが容易に推定できた。

【００５５】

【発明の効果】以上、この発明の排ガス除害装置は、有機化合物溶液原料を用いたＣＶＤ反応炉の排気部に接続され、前記排気部から排出されたガスが少なくとも還元剤及びアルカリ剤が配置された処理部を通過するように構成したので、また、還元剤を金属粉、亜硫酸塩、スズ塩及び第１鉄塩の中から選ばれた少なくとも１種にし、アルカリ剤を、アルカリ金属ケイ酸塩、アルカリ金属炭酸塩、アルカリ金属アルミン酸塩及びアルカリ金属酸化物の中から選ばれた少なくとも１種にし、これら、還元剤及びアルカリ剤を１５０～３００℃に加熱したので、排ガスの除害効率が向上するとともに、除害装置内での目詰まり等の問題が低減し、除害装置の処理能力が維持され、除害処理寿命も延長されるという効果を奏する。

【００５６】さらに、上記排ガス除害装置において、還元剤及びアルカリ剤の配置された処理部の少なくとも後段に酸化触媒が配置された第２の処理部を備えた、酸化触媒を、Pt、Pdのうちの少なくとも一種及び／またはFe、Mn、Ni、Co、Cu及びCrから選ばれた少なくとも１種とし、２５０～４５０℃に加熱したので、より一層、排ガスの除害効率が向上する。

【００５７】上記、排ガス除害装置において、前段のＣＶＤ反応炉で用いられる有機化合物溶液原料として、テトラヒドロフランに有機化合物が溶解された溶液を用いた場合、従来の排ガス除外装置で処理するよりも優れた＊除害効果を奏する。

【図面の簡単な説明】

【図１】本発明の排ガス除害装置の構成を説明するためのも模式図である。

【図２】本発明の排ガス除害装置における還元剤及びアルカリ剤処理部の構成を示した図である。

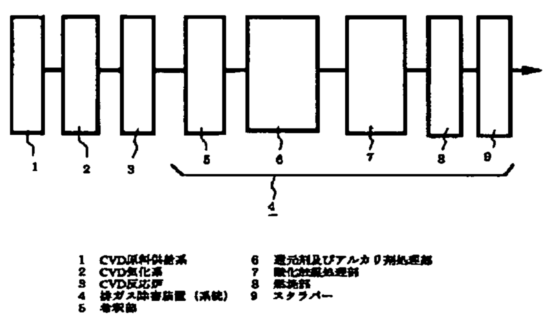
【図３】本発明の排ガス除害装置における還元剤及びアルカリ剤処理部ならびに酸化触媒処理部の構成を示した図である。

【図４】従来の排ガス除害装置の一般的な構成例を示した図である。

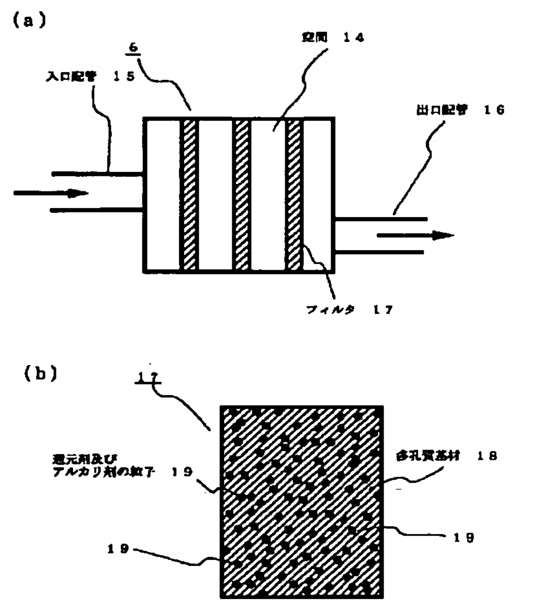
【符号の説明】

１　ＣＶＤ原料供給系、　２　ＣＶＤ気化系、　３　ＣＶＤ反応炉、４　排ガス除害装置（系統）、　５　希釈部、還元剤及びアルカリ剤処理部、　７　酸化触媒処理部、　８　燃焼部、９　スクラバー、１４　反応部内の空間、　１５　処理部６への入り口配管、１６　処理部６からの出口配管、１７　処理部６の内部に設置されたフィルタ、　１８　多孔質基材、１９　還元剤及びアルカリ剤の粒子、　２０　処理部６への入り口配管、２１　接続配管、　２２　処理部７の内部に設置されたフィルタ、２３　処理部７からの出口配管。

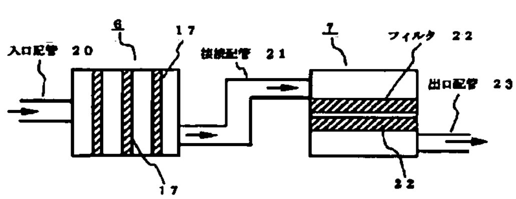
【図１】



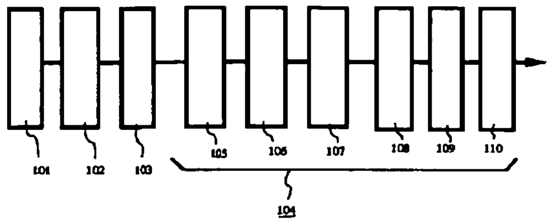
【図２】



【図３】



【図４】



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